ANHARMONIC OSCILLATORS IN QUANTUM MECHANIC

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ANHARMONIC OSCILLATORS IN QUANTUM MECHANIC

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CERTIFICATE

Certified that the work presented in this thesis entitled: 'Anharmonic Oscillators in Quantum Mechanics', by Subodh Prakash Bhatnagar has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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SYNOPSIS

Thesis entitled : ANHARMONIC OSCILLATORS IN QUANTUM MECHANICS, submitted by SUBODH P. BHATNAGAR to the Department of Physics, Indian Institute of Technology Kanpur, in partial fulfilment of the requirement of the Ph.D. degree.

In this work the following eigenvalue problems have been investigated:

(i) the quartic anharmonic oscillator (Hamiltonian $H=p^2+x^2+\lambda x^4$, $p = -i\frac{d}{dx}$, $\lambda > 0$) and the associated problem of the pure quartic oscillator ($H = p^2 + \lambda x^4, \lambda > 0$),

(ii) the general anharmonic oscillators ($H = p^2 + x^2 + \lambda x^{2\mu}$, $\lambda > 0$, $\mu = 3,4,\ldots$),

(iii) the double minimum oscillator ($H = p^2 - x^2 + \lambda x^4$, $\lambda > 0$).

Eigenvalues and eigenfunctions of these systems are obtained in all regimes of the quantum number n and the anharmonicity constant λ. The computed eigenfunctions are then used to obtain the transition moments. The eigenvalues reported in this work are accurate to 15 significant figures and the transition moments to 12 figures.

The eigenvalues of the anharmonic oscillators ($H = p^2 + x^2 + \lambda x^{2\mu}$) fall into two distinct classes (Hioe et al. 1976). In the low n, low λ regime the eigenvalues differ slightly from the harmonic oscillator levels whereas in the high n, high λ regime they differ slightly from the

pure anharmonic oscillator ($H = p^2 + \lambda x^{2\mu}$) eigenvalues. Between these two regimes lies the 'boundary layer' in which the eigenvalues are neither 'near harmonic' nor near 'pure anharmonic'. The existence of different regimes implies different oscillation properties of the corresponding eigenfunctions. We assert that this fact must be explicitly included in solving the eigenvalue problem. The method applied in this work (Banerjee 1976) involves the use of an appropriately (according to regime) scaled basis for the expansion of each eigenfunction. The appropriately scaled basis simulates the different oscillation properties of the eigenfunctions in different regimes and makes possible a uniform treatment of the problem in all regimes.

The Chapter I of the thesis is a review of various earlier methods used to solve the anharmonic oscillator eigenvalue problem. These methods are suitable only in a particular regime of (n,λ) and do not give eigenvalues to the same accuracy when extended to other regimes. The construction of an appropriately scaled basis and the method used in this thesis for the computation of the eigenvalues is described in Chapter II. The actual computation of the eigenvalues is reduced to the determination of the roots of a transcendental equation in the energy. This is done numerically. Accurate eigenvalues and eigenfunctions of the quartic anharmonic and the pure quartic oscillator are

then obtained for various values of (n,λ) covering all different regimes. In Chapter III we show that the eigenvalue problem of the general anharmonic oscillators may be solved for any μ in all regimes of (n,λ) using the same method. In Chapter IV accurate eigenvalues and eigenfunctions of the double minimum oscillator are calculated. A WKB expression for the splitting between the lower eigenvalues, bunched in pairs, is obtained and the WKB values are compared with the corresponding accurate values. In Chapter V, the transition moments which are the matrix elements of x^k (k = integer) between the anharmonic oscillator eigenstates are calculated using the computed eigenvalues and eigenfunctions. The transition moments for any particular transition satisfy an exact linear recurrence relation (Banerjee 1977) from which the higher moments for that transition may be obtained recursively, without integration.

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CHAPTER I

INTRODUCTION

The study of anharmonic oscillators is a subject of very general interest. The quartic anharmonic oscillator described by the Hamiltonian $H = p^2 + x^2 + \lambda x^4$ ($\lambda > 0$ is the anharmonicity constant) is the simplest example of nonlinear oscillation in classical mechanics (Krylov and Bogoliubov 1943). The investigation of the same problem in quantum mechanics is useful as a model problem in molecular physics and field theory In molecular vibrations, the potential functions are quite often of the mixed harmonic-quartic type. Indeed, in some cases of interest, due to accidental cancellation of the quadratic terms, the potential functions become nearly pure quartic (see Chan and Stelman 1963, Reid 1970). The quartic anharmonic oscillator is of particular interest in field theory because it is a model of $\lambda\phi^4$ quantum field theory in one-dimensional space-time. The investigations from the field theory point of view are referred to in the work of Bender and Wu (1976). A general account on the anharmonic oscillator problem may be found in Hioe and Montroll (1975) and Hioe, MacMillen and Montroll (1976).

There have been persistent attempts for finding the eigenvalues of the quartic anharmonic oscillator since the beginning of quantum mechanics. In the earliest attempts the formal Rayleigh Schrödinger perturbation method was applied to solve this eigenvalue problem in which the λx^4 term was considered as the perturbation on the harmonic oscillator Hamiltonian $H_0 = p^2 + x^2$. Bender and Wu (1969) calculated nearly 70 expansion coefficients of the perturbation series in powers of λ for the ground state energy and observed an unexpected rapid increase in their magnitudes. A detailed analysis then revealed that the perturbation series for the eigenvalues in powers of λ is not convergent for any positive value of λ, no matter how small. Bender and Wu (1969) studied the analytic properties of the eigenvalues $E_n(\lambda)$ (n being the quantum number) in the complex λ plane and showed that there is a third order branch point at $\lambda = 0$. It was further observed that $\lambda = 0$ is not an isolated singularity but is a limit point of an infinite number of branch points of $E_n(\lambda)$. Simon (1970) proved the above properties of $E_n(\lambda)$ by more rigorous and technically sound arguments. In the language of perturbation theory the nonanalyticity of $E_n(\lambda)$ implies that the perturbation series of $E_n(\lambda)$ in powers of λ is non-convergent.

The following scaling argument due to Symanzik is significant in this connection. On performing the scaling

transformation $x \to ax$, $p \to a^{-1}p$ on the Hamiltonian $H(k,\lambda) = p^2+kx^2+\lambda x^4$ we obtain

$$H(k,\lambda) = \frac{1}{a^2}H(a^4k,\ a^6\lambda)\ . \tag{1.1}$$

Since the above scaling transformation is implementable by unitary transformation, the two sides of eqn. (1.1) have identical eigenvalues. The relation (1.1) thus ensures that the eigenvalue problem of the quartic anharmonic oscillator may be completely described in terms of the reduced Hamiltonian $H(1,\lambda) = p^2 + x^2 + \lambda x^4$. Setting $a^6 = 1/\lambda$, one obtains

$$E_n(1,\lambda) = \lambda^{1/3}\ E_n(\lambda^{-2/3},1)\ . \tag{1.2a}$$

Hence,

$$E_n(1,\lambda) \sim \lambda^{1/3}\ E_n(0,1) \text{ as } \lambda\to\infty\ . \tag{1.2b}$$

Since $E_n(0,1)$ is independent of λ, $E_n(1,\lambda) \sim C_n\ \lambda^{1/3}$ for large λ.

The difficulties in perturbation approach may also be seen if one considers the equation $H\psi = E\psi$ in momentum representation (Hioe and Montroll 1975):

$$\left(\lambda\frac{d^4}{dp^4} - \frac{d^2}{dp^2} + p^2\right)\ \psi = E\ \psi\ . \tag{1.3}$$

The perturbation parameter λ appears here as the coefficient of the highest derivative. It is well known that the expansion of the solutions of such differential equation

in power series of the small parameter is non-convergent (VanDyke 1964). It is therefore not so surprising that the Rayleigh Schrödinger perturbation expansion of the anharmonic oscillator eigenvalues in powers of λ fails to converge. The perturbation treatment of this problem in classical mechanics is instructive in this connection. It consists of obtaining approximate solutions with the help of the expansion of the displacement in power series of the anharmonicity constant. It leads to solutions that contain secular terms like $t^m \sin \alpha t$, $t^m \cos \alpha t$ in which the time 't' appears outside the sine and cosine symbols. The secular terms in a finite term expansion introduce non-periodic solutions and cause the calculated displacements to become arbitrarily large at large t. Further, the total energy becomes a function of time, violating the energy conservation principle (Bogoliubov and Mitropolsky 1961). The difficulties arising in the quantum mechanical perturbation expansion may be viewed in this context.

A detailed analysis of the perturbation series of $E_n(\lambda)$ shows that it is asymptotic in nature (Simon 1970). Such series are usually summed uniquely through various summability techniques such as Stieltjes Padé or Borel methods. Loeffel et al. (1969) have proved that the perturbation series sums under Padé approximation to the actual eigenvalue. The Padé approximation in general

consists of replacing the power series by a sequence of rational functions $f(M,N)$ of the form of a polynomial of degree M divided by another polynomial of degree N. Simon (1970) calculated the ground state energy by this approximation for various values of λ. His results show that the Padé approximants converge quickly for $0 < \lambda < 1$ but for $\lambda > 1$ the rate of convergence is not very good. Graffi et al. (1970) described how improved values of $E_C(\lambda)$ can be obtained by using Padé approximants to the Borel summability method. Reid (1967) showed that the perturbation series can also be summed by converting it into equivalent continued fraction and obtained the ground state as well as a few excited state eigenvalues for various values of λ. The agreement of the eigenvalues obtained from these various summability methods with the corresponding accurate eigenvalues is found to be poor unless n and λ are sufficiently small. The scope of these methods is therefore limited to small n, small λ values only.

Various variational and numerical methods have been widely employed by many authors either to the quartic anharmonic oscillator problem or to the associated problem of the pure quartic oscillator ($H = p^2 + \lambda x^4, \lambda > 0$). Calculations are generally done in the harmonic oscillator basis $\{x^m e^{-x^2/2}\}$ and the usual technique is to truncate and diagonalize a large but finite matrix. Results of such

calculations are summarised in Table (I.1). They differ from one another either in the method of diagonalization or in the size of the basis used. Some calculations for upper and lower bounds of first few eigenvalues with varying anharmonicity were done by Bazley and Fox (1961) and Reid (1965). The procedure for lower bounds used by Bazley and Fox was to construct intermediate Hamiltonians H^k such that $H^o < H^1 < H^2 \ldots < H$ and to determine eigenvalues of successive H^k. Reid used the method of Löwdin (1965) for obtaining the lower bounds. The upper bounds were calculated by employing the usual Rayleigh-Ritz variational approach. It may be noted that in these calculations the gap between the upper and the lower bounds increases rapidly on increasing n or λ (e.g. in Reid's work the gap, which is $O(10^{-15})$ for $E_0(\lambda = 0.25)$, becomes $O(10^{-1})$ for $E_9(\lambda = 1.0)$).

Biswas et al. (1973) used the 'Hill determinant' method to obtain first eight eigenvalues of the quartic anharmonic oscillator for values of λ in the range $0 < \lambda \leq 100$. They used an expansion in terms of the functions $\{x^m e^{-x^2/2}\}$ for the eigenfunctions and obtained eigenvalues by finding the roots of a sequence of characteristic polynomials in E. The polynomials corresponded to various order truncations of the Hill determinant. For higher eigenvalues or for higher λ the numerical errors in their work become too severe

TABLE (I.1): Comparison of the Results of Various Variational and Numerical Methods.

Authors	Year	System	No. of basis functions used	n	λ	Accuracy of $E_n(\lambda)$ and other remarks
McWeeny and Coulson	1948	Quartic Oscillator	8	0 to 4	1.0	7 figures for E_0, 5 figures for E_4
Chan and Stelman	1963	''	50	0 to 19	1.0	8 significant figures (for $n \geq 17$ $E_n(\lambda)$ are inaccurate in last 3-4 figures)
Vescelius and Neff	1968	''	-	0 to 19	1.0	6 to 8 significant figures (the method uses continued fraction technique)
Bell et al.	1970	''	800	0 to 49	1.0	7 to 9 significant figures (for $n > 17$ $E_n(\lambda)$ are inaccurate in last figures)
Reid	1970	''	100	0 to 23	1.0	12 significant figures
Bazley and Fox	1961	Quartic Anharmonic oscillator	5	0,2,4, ...10	0.1 to 1.0	5-6 significant figures for E_0, none for E_8
Chan, Stelman and Thompson	1964	''	20	0 to 9	-	4-5 significant figures for lower eigenvalues, 1-2 significant figures for higher eigenvalues.
Reid	1965	''	20	0 to 9	0.1 to 1.0	15 significant figures for E_0 ($\lambda = 0.25$), 2 significant figures for E_9 ($\lambda = 1.0$)
Biswas et al.	1973	''	-	0 to 7	0.1 to 100	14 significant figures for E_0 8-9 significant figures for $n \geq 1$.

The results of the variational and numerical calculations show that these methods are suitable for the evaluation of a few lower eigenvalues and for moderate anharmonicities. The accuracy of the results is seriously affected on increasing n or λ and is not necessarily improved by increasing the size of the basis. Further, the eigenfunctions obtained from variational calculations are far less accurate than the corresponding eigenvalues. Evaluation of matrix elements of operators using such eigenfunctions is not expected to yield values of known or definite accuracy.

The WKB method has been used for obtaining approximate eigenvalues for high n. In the WKB approximation (Titchmarsh 1961),

$$E_n(0,1) = C\ (n + \tfrac{1}{2})^{4/3}, \quad C = 2^{2/3}(1.376) \quad (1.4)$$

It is known from eqn. (1.2b) that the quartic anharmonic oscillator eigenvalues $E_n(1,\lambda) \simeq \lambda^{1/3}\, E_n(0,1)$ in the large λ limit. Hence, for large n, large λ –

$$E_n(1,\lambda) \simeq C\ \lambda^{1/3}\ (n + \tfrac{1}{2})^{4/3} \ . \quad (1.5)$$

A more sophisticated WKB expression for $E_n(1,\lambda)$ is obtained by Hioe and Montroll (1975); see eqn. (1.6.c) later.

The most comprehensive work on the anharmonic oscillators is due to Hioe and Montroll (1975) and Hioe et al. (1976 They distinguished two limiting regimes of values of n and λ.

In one regime the energy eigenvalues differ slightly from the harmonic oscillator levels; in the other they differ slightly from the pure quartic oscillator eigenvalues. These regimes are called the 'near harmonic' regime and the 'near quartic' regime, respectively. Between these two regimes lies the 'boundary layer' in which the eigenvalues are neither 'near harmonic' nor 'near quartic'. They developed fast converging algorithms for computing the eigenvalues in small n regime by writing the eigenvalue problem in Bargmann representation and solving the associated difference equation. The eigenvalues were thus computed to 8-9 significant figures for n = 0, 1, ... 8 and for values of λ in the range $.004 \leq \lambda \leq 40000$. They also constructed several simple formulae for $E_n(\lambda)$ with different ranges of validity which when combined give good approximations (about 8 significant figures) to $E_n(\lambda)$ except in the 'boundary layer'. The formulae with their ranges of validity are as follows:

(a) For the near harmonic regime

$$E_n(\lambda) = (2n+1) + \frac{3}{4}\lambda\,\{1+2n(n+1)\} - \lambda^2\left\{ \frac{(n+1)(n+\frac{3}{2})^2(n+2)}{[4+3\lambda(2n+3)]} + \frac{(n+1)(n+2)(n+3)(n+4)}{32[4+3\lambda(2n+5)]} - \frac{n(n-\frac{1}{2})^2(n-1)}{[4+3\lambda(2n-1)]} - \frac{n(n-1)(n-2)(n-3)}{32[4+3\lambda(2n-3)]}\right\} + 0(\lambda^3) \qquad (1.6a)$$

(b) For small n, large λ region

$$E_n(\lambda) = \lambda^{1/3} [\varepsilon_n + \alpha_n \lambda^{-2/3} + \beta_n \lambda^{-4/3} + \ldots], \quad (1.6b)$$

where the constants ε_n, α_n and β_n were determined by fitting eqn. (1.6b) to the numerical values of $E_n(\lambda)$ for each state up to n=10.

(c) For large n, large λ region

$$E_n(\lambda) = \lambda^{1/3} [c\{ (n+\tfrac{1}{2}) + \frac{\delta}{(n+\frac{1}{2})} \}^{4/3} + a(n+\tfrac{1}{2})^{2/3} \lambda^{-2/3} + b\, \lambda^{-4/3} + \ldots] . \quad (1.6c)$$

The above expression results from a detailed investigation of the WKB approximation formula and consists of expanding the elliptic integrals in the WKB formula in a series in E_n; the constants c, a and b are identified from this expansion. It may be mentioned here that Mathews and Eswaran (1972) also obtained some approximate formulae through a semiclassical treatment.

Recently, Mathews and Govindarajan (1977) used a 'residue squaring method' for the iterative diagonalization of the quartic anharmonic oscillator Hamiltonian in which the λx^4 term is assumed to be a perturbation on the rest. In this work the off diagonal part (of order λ compared to the diagonal part) is successively reduced to orders λ^2, λ^4, λ^8, ... They obtained four lowest even parity eigenvalues and an approximate analytic formula for $E_n(\lambda)$, similar to the

equation (1.6a), which gives good approximations to the eigenvalues in the near harmonic regime.

It is seen from the above discussion that the various methods, which have been applied to solve the anharmonic oscillator eigenvalue problem, are suitable only in some particular regime of (n,λ) and do not give eigenvalues to the same accuracy when extended to other regimes. Moreover, they do not yield accurate eigenfunctions. In contrast, we use a method (Banerjee 1976) to obtain the eigenvalues of the quartic anharmonic oscillator which applies with uniform and arbitrarily high accuracy for all values of n and λ. The method also yields eigenfunctions of accuracy comparable with that of the eigenvalues which are used for the computation of high accuracy matrix elements. In the next chapter the method is described and the eigenvalues and the eigenfunctions of the quartic anharmonic oscillator and the associated problem of the pure quartic oscillator are obtained. The eigenvalues, accurate to 15 significant figures, are presented for various values of (n,λ) covering all the different regimes. We show in Chapter III that the method may be extended to solve general anharmonic oscillator ($H = p^2 + x^2 + \lambda x^{2\mu}$, $\mu = 3,4, \ldots$) eigenvalue problem. Eigenvalues of the sextic (μ=3) and the octic (μ=4) anharmonic oscillators are thus obtained accurate to 15 significant figures in all regimes of (n,λ). In Chapter IV the eigenvalue

spectrum of the double minimum oscillator ($H = p^2-x^2+\lambda x^4$, $\lambda > 0$) is investigated. The lower eigenvalues of the double minimum oscillator are closely bunched in pairs for small λ. These eigenvalues have been evaluated accurately using the same method. A WKB expression for the splitting between the eigenvalues bunched in pairs is obtained and the WKB values are compared with the corresponding accurate values. In Chapter V the transition moments between the anharmonic oscillator energy eigenstates are obtained from the computed eigenvalues and eigenfunctions. Further, the multipole transition moments are shown to satisfy an exact linear recurrence relation which is valid for any polynomial potential.

CHAPTER II

THE QUARTIC ANHARMONIC OSCILLATOR

In this chapter we determine accurate eigenvalues and eigenfunctions of the quartic anharmonic oscillator ($H = p^2 + x^2 + \lambda x^4$, $\lambda > 0$, $p = -i \frac{d}{dx}$) for various values of the quantum number n and the anharmonicity constant λ. The existence of two distinct regimes of values of (n, λ), namely the 'near harmonic' and the 'near quartic', separated by a 'boundary layer' implies different oscillation properties of the corresponding eigenfunctions. We assert that this fact must be explicitly included in solving the eigenvalue problem. Following Banerjee (1976), it is shown in the next section that the basis functions (used in the solution of the eigenvalue problem) may be appropriately scaled to simulate the oscillation properties of the eigenfunctions in all regimes.

II.1 Scaling and the Appropriate Scaling Formula

The eigenfunctions $\psi_n(x; \lambda)$ may be expanded in the basis $\{x^m e^{-\alpha x^2}\}$ as:

$$\psi_n(x, \lambda) = e^{-\alpha x^2} \sum_{m=0}^{\infty} a_m x^m, \qquad (2.1)$$

where the scaling is introduced through the parameter 'α'. For an effective expansion the scaling α is chosen such that a sufficient number of the lower members of the basis functions (at least n for the n-th state) have their main contribution in the region of oscillation and outside it they decay monotonically Since the region of oscillation depends on n and λ, the scaling α also depends on n and λ. A simple criterion for the appropriate scaling is obtained as follows: The region of oscillation for the n-th eigenfunction of the quartic anharmonic oscillator (for sufficiently large n) $\sim(E_n/\lambda)^{1/4}$. In the WKB approximation $E_n(\lambda) \approx C\lambda^{1/3}(n+\frac{1}{2})^{4/3}$. Therefore the region of oscillation $\sim\lambda^{-1/6}(n+\frac{1}{2})^{1/3}$. The exact n-th eigenfunction has n zeros in the region of oscillation. Hence setting the region of oscillation for the n-th eigenfunction equal to the width of the n-th basis function ($\sim\sqrt{(n/\alpha)}$) we obtain

$$\alpha(n,\lambda) \sim (n+\tfrac{1}{2})^{1/3}\,\lambda^{1/3}.$$

This puts the span of the first n (or a number proportional to n) basis functions in the region of oscillation of the n-th eigenfunction <u>for all n and λ</u>, just as required for an effective expansion. In view of the WKB estimate and the large λ assumption implicit in the derivation of the above scaling formula, it is not expected to be good when n and or λ is small. However, for $\lambda \to 0$ or for small n the

scaling must approach the value 1/2 appropriate for the harmonic oscillator. Hence the scaling formula for all regimes of (n,λ) is

$$\alpha(n,\lambda) = \frac{1}{2} + (n + \frac{1}{2})^{1/3} \lambda^{1/3} . \tag{2.2}$$

The effect of using an appropriately scaled basis is remarkable. It is now possible to compute the eigenvalues in any regime of (n,λ) with arbitrarily high accuracy.

It is to be noted that the different regimes of (n,λ) are distinguished according to the above scaling formula. Thus

$(n + \frac{1}{2})^{1/3} \lambda^{1/3} \ll \frac{1}{2}$ is the near harmonic regime,

$(n + \frac{1}{2})^{1/3} \lambda^{1/3} \gg \frac{1}{2}$ is the pure quartic regime,

$(n + \frac{1}{2})^{1/3} \lambda^{1/3} \simeq \frac{1}{2}$ is the boundary layer between the above two regimes.

The value of the combination $(n + \frac{1}{2})\lambda$ is seen to determine the regime to which an eigenvalue belongs. The importance of the above combination of n and λ in determining the various regimes was also recognised by Hioe et al. (1976) on essentially empirical grounds. It is in this work that the combination $(n + \frac{1}{2})\lambda$ is shown to determine the characteristic scaling in a given regime of (n,λ) through the relation (2.2). This observation leads to the construction of a scale adapted

basis and makes possible a uniform treatment of the problem in all regimes of (n,λ).

II.2 Method

The method applied for obtaining the eigenvalues is described in this section. The Schrödinger equation for the quartic anharmonic oscillator is

$$[-\frac{d^2}{dx^2} + x^2 + \lambda x^4]\ \psi(x;\lambda) = E(\lambda)\ \psi(x;\lambda), \qquad (2.3)$$

where the eigenfunctions $\psi_n(x;\lambda) \to 0$ as $x \to \pm\infty$. The expansion (2.1) on substitution into the above equation yields the following 4-term linear recurrence relation, connecting the alternate expansion coefficients $\{a_m\}$,

$$(m+1)(m+2)\ a_{m+2} + (E-4\alpha m-2\alpha)\ a_m + (4\alpha^2-1)\ a_{m-2} - \lambda\, a_{m-4} = 0 . \qquad (2.4)$$

The above recurrence relation may be rewritten in the following notations:

$$a_{m+2} + d_{m,m}a_m + d_{m,m-2}a_{m-2} + d_{m,m-4}a_{m-4} = 0,$$

where

$$d_{m,m} = \frac{(E - 4\alpha m-2\alpha)}{(m+1)(m+2)}\ , \ d_{m,m-2} = \frac{(4\alpha^2-1)}{(m+1)(m+2)}\ ,$$

$$d_{m,m-4} = - \frac{\lambda}{(m+1)(m+2)}\ . \qquad (2.5)$$

Since the Hamiltonian for the system has even symmetry, the solutions of the Schrödinger equation are either even or odd functions of x. The even and odd parity solutions are obtained respectively by assigning the initial conditions (i) $a_0=1$, $a_1=0$ (ii) $a_0=0$, $a_1=1$. The recursion(2.5) may be viewed as an infinite set of linear homogeneous equations in the unknowns $\{a_m\}$. For the self consistency the infinite determinant $\Delta(E)$ formed from the coefficients of $\{a_m\}$ must vanish. It gives

$$\Delta(E)=\begin{vmatrix} d_{00} & 1 & 0 & .. & & & & \\ d_{20} & d_{22} & 1 & 0 & .. & & & \\ d_{40} & d_{42} & d_{44} & 1 & 0 & .. & & \\ 0 & d_{62} & d_{64} & d_{66} & 1 & 0 & .. & \\ .. & .. & .. & .. & .. & .. & .. & .. \\ .. & 0 & d_{m,m-4} & d_{m,m-2} & d_{m,m} & 1 & 0 & .. \\ .. & .. & .. & .. & .. & .. & .. & .. \end{vmatrix}=0.(2.6)$$

The roots of the above transcendental equation are the eigenvalues. This mode of writing the characteristic equation in the form of an infinite determinant is well known from the eigenvalue problem associated with Hill's equation (Whittaker and Watson 1927). Denoting the truncated determinant formed by omitting all rows and columns beyond the element $d_{m,m}$ as $\Delta_{m+2}(E)$, it may be noted that $\Delta_m(E)$ is a polynomial in E

of degree m/2 when m is even and (m-1)/2 when m is odd. The zeros of $\Delta_m(E)$, $\Delta_{m+2}(E)$, ... are numerically stable for large m provided the scaling α is appropriate. The determinant $\Delta_m(E)$ for $m\to\infty$ defines $\Delta(E)$. Hence the problem of obtaining the eigenvalues is reduced to finding the zeros of $\Delta_m(E)$ for sufficiently large m. The zeros of $\Delta_m(E)$ are obtained numerically by Newton's method which requires an initial estimate of the required zero say $E_{initial}$ as well as the values of $\Delta_m(E)$ and $\Delta'_m(E)$ $(= \partial\Delta_m/\partial E)$ at $E = E_{initial}$. To evaluate $\Delta_m(E)$ we note that the truncated determinants satisfy the following 4-term linear recurrence relation

$$\Delta_{m+2}(E) - d_{m,m}(E)\,\Delta_m(E) + d_{m,m-2}\,\Delta_{m-2}(E) - d_{m,m-4}\,\Delta_{m-4}(E) = 0, \tag{2.7}$$

obtained by expanding the determinant $\Delta_{m+2}(E)$. The value of the determinants $\Delta_m(E)$ may thus be computed successively upto any order in terms of Δ_0(or Δ_1) using (2.7). The recurrence relation (2.7) on differentiation with respect to E yields

$$\Delta'_{m+2}(E) - d'_{m,m}\,\Delta_m(E) - d_{m,m}(E)\,\Delta'_m(E) + d_{m,m-2}\,\Delta'_{m-2}(E)$$

$$- d_{m,m-4}\,\Delta'_{m-4}(E) = 0, \tag{2.8}$$

from which $\Delta'_m(E)$ may be computed upto any order recursively. The recursions (2.7) and (2.8) are numerically stable. The initial estimates for the eigenvalues required in the Newton's method may be obtained for low n by evaluating a

sufficiently large order determinant $\Delta_M(E)$ from the recursion (2.7) at various E points. Opposite signs of $\Delta_M(E)$ for two neighbouring E values indicate that an eigenvalue is crossed which provides sufficiently accurate estimate for the Newton's method. For high n (and not too low λ) the corresponding WKB approximations of the eigenvalues are good initial estimates. The procedure for obtaining initial estimates in the (high n, low λ) region of the 'boundary layer' is described in Appendix A.

The actual computation of the eigenvalues may now be performed in the following manner. An initial estimate ($E = E_{initial}$) is fed into the recursions (2.7) and (2.8) containing the appropriate value for α. The recursions are then continued on a computer until the corrections, given by the Newton's formula

$$\delta E(m) = -\{ \Delta_m(E)/\Delta_m'(E)\}_{E=E_{initial}}, \qquad (2.9)$$

stabilize to a prescribed extent (see Wilkinson 1965). The corrected value for E is then fed back in the second step as the initial value. This is continued till the required accuracy in the computed eigenvalues is reached. Due to the quadratic convergence of Newton's method it is possible to refine a rather crude initial estimate for an eigenvalue (say, within a few percent) to a 15 figure accuracy in 4 or 5 steps for all eigenvalues. Some typical examples to

elucidate this are given in Table (II.1).* In principle, the method can be carried to an arbitrary high accuracy. The accuracy of the computation is limited only by the precision of the arithmetic used (16 significant figures in IBM 7044).

II.3 Eigenvalues

Very accurate eigenvalues of the quartic anharmonic oscillator and the associated problem of the pure quartic oscillator ($H = p^2 + \lambda x^4, \lambda > 0$) have been obtained using the method described in the previous section and the scaling formula

$$\alpha(n,\lambda) = \frac{1}{2} + (1.2 \text{ to } 1.4)\ (n + \tfrac{1}{2})^{1/3}\, \lambda^{1/3}. \quad (2.10)$$

The constant within the bracket (1.2 to 1.4) has been set empirically by finding the values of the scaling α for which the computed eigenvalues stabilize the earliest. The constant (1.2 to 1.4) is found to work admirably in the entire range of (n,λ). The calculation of the eigenvalues for the pure quartic oscillator is similar to that done for the quartic anharmonic oscillator. The only difference is in the value of $d_{m,m-2}$ in equations (2.5) to (2.8), which in the pure quartic oscillator case is equal to $(4\alpha^2/(m+1)(m+2))$. The computations were done on IBM 7044 computer using double precision arithmetic (16 digits mantissa). The eigenvalues were evaluated to

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* Tables referred to in any chapter are given at the end of that chapter.

16 significant figures and then rounded off to 15 figures for the Tables.

The eigenvalues of the quartic anharmonic and the pure quartic oscillator for various values of (n, λ) covering all regimes are listed in Tables (II.2 to II.5). In Table (II.2) we compare our results of $E_n(\lambda=1)$ for n=0, 10, 100, 1000 and 10000 with the corresponding results of various earlier calculations. In Table (II.3) the first 50 eigenvalues of the quartic anharmonic and the pure quartic oscillators are given for $\lambda=1$. The eigenvalues for any other value of λ in the case of pure quartic oscillator can be obtained from the corresponding values for $\lambda=1$ through the exact scaling relation $E_n(\lambda) = \lambda^{1/3}E_n(1)$. For the quartic anharmonic oscillator different eigenvalues for various values of λ between .00001 and 40000 were computed, and are presented in the Table (II.4). It includes the eigenvalues for the (high n, low λ) region of the 'boundary layer'. The computation of eigenvalues in this region of the boundary layer is found to be the most difficult in the earlier literature. None of the approximation formulae (1.6a,b,c) constructed by Hioe et al. (1975) are adequate for this (high n, low λ) region. In the present work the eigenvalues in this region (e.g. eigenvalues corresponding to $n=100$, $\lambda=10^{-4}$ and $n=1000$, $\lambda=10^{-3}$ in Table (II.4)) are obtained by the same technique and with the same accuracy as any other,

highlighting the scope of computations with an appropriately scaled basis. In Table (II.5) we focus on the regimes of extreme values of (n,λ). Hioe et al. (1975, 1976) give different formulations of the eigenvalue problem in each of these regimes which cannot be extended into other regimes because of the boundary layer in between. In contrast, we have obtained eigenvalues in each of these regimes by the same formulation and with the same accuracy.

II.4 Stability of Zeros of $\Delta_m(E)$

The recursive evaluation of the determinants $\Delta_m(E)$ and the stability of their zeros will now be considered in some detail. It may be noted that the recursion (2.7) is obtainable from the recursion (2.5) by replacing a_m with Δ_m and changing the sign of every alternate term. This prescription is valid when the coefficient of the highest order term in the $\{a_m\}$ recursion is set unity (by properly dividing, if necessary). Then

$$\begin{aligned} \Delta_m &= (-1)^{m/2}\, a_m\,, \quad m = 0,2,4,\ldots, \\ \Delta_m &= (-1)^{(m-1)/2} a_m, \quad m=1,3,5,\ldots\ . \end{aligned} \tag{2.11}$$

In the case when the coefficient of the highest order term is not unity, the $\{a_m\}$ recursion is

highlighting the scope of computations with an appropriately scaled basis. In Table (II.5) we focus on the regimes of extreme values of (n,λ). Hioe et al. (1975, 1976) give different formulations of the eigenvalue problem in each of these regimes which cannot be extended into other regimes because of the boundary layer in between. In contrast, we have obtained eigenvalues in each of these regimes by the same formulation and with the same accuracy.

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In the case when the coefficient of the highest order term is not unity, the $\{a_m\}$ recursion is

$$d_{m,m+2}\,a_{m+2} + d_{m,m}a_m + d_{m,m-2}a_{m-2} + d_{m,m-4}a_{m-4} = 0\,. \qquad (2.12)$$

The corresponding infinite determinant formed in this case is

$$\bar{\Delta}(E) = \begin{vmatrix} d_{00} & d_{02} & 0 & \cdot\cdot & & & & \\ d_{20} & d_{22} & d_{24} & 0 & \cdot\cdot & & & \\ d_{40} & d_{42} & d_{44} & d_{46} & 0 & \cdot\cdot & & \\ 0 & d_{62} & d_{64} & d_{66} & d_{68} & 0 & \cdot\cdot & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot\cdot & \cdot\cdot \\ \cdot\cdot & 0 & d_{m,m-4} & d_{m,m-2} & d_{m,m} & d_{m,m+2} & 0 & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \end{vmatrix}\,. \qquad (2.13)$$

The truncated determinants $\bar{\Delta}_{m+2}(E)$ formed by omitting all rows and columns beyond the element $d_{m,m}$ in $\bar{\Delta}(E)$ may be expanded in terms of the truncated determinants of lower orders. It provides the following 4-term recurrence relation,

$$\bar{\Delta}_{m+2}(E) - d_{m,m}\,\bar{\Delta}_m(E) + d_{m-2,m}d_{m,m-2}\,\bar{\Delta}_{m-2}(E)$$

$$- d_{m-4,m-2}d_{m-2,m}d_{m,m-4}\,\bar{\Delta}_{m-4}(E) = 0\,. \qquad (2.14)$$

The determinants $\{\bar{\Delta}_m(E)\}$ are related to $\{\Delta_m(E)\}$ by

$$\bar{\Delta}_m(E) = d_{m-2,m}\,d_{m-4,m-2}\,\cdots\,d_{02}\,\Delta_m(E),\quad m=0,2,4,\ldots\,,$$

$$(2.15)$$

$$\bar{\Delta}_m(E) = d_{m-2,m}\,d_{m-4,m-2}\,\cdots\,d_{13}\,\Delta_m(E)\,,\quad m=1,3,5,\ldots\,.$$

The asymptotic behaviour of the solution of the Schrödinger equation (2.3) $\sim \exp(\pm|x|^3/3)$. It requires

$$a_{m+2}/a_{m-4} \sim \lambda/m^2 , \quad m \to \infty , \tag{2.16}$$

in the series solution (2.1). It follows immediately from the relation (2.11) that for the determinants $\{\Delta_m\}$ it is required that

$$\Delta_{m+2}/\Delta_{m-4} \sim -\lambda/m^2 , \quad m \to \infty . \tag{2.17}$$

We observe during the recursive evaluation of the value of $\Delta_{m+2}(E)$ that for sufficiently large m the second and third terms in the recursion (2.7) become order of magnitudes smaller than the last term and the asymptotic dependence (2.17) is satisfied. The asymptotic relation (2.17) implies a sequence of decreasing determinants beyond a sufficiently large m. This zeroing for large m must be isolated from the determination of the eigenvalues which are the zeros of $\Delta(E)$ for values of E. It is possible to achieve this quite simply by redefining the determinants $\Delta_m(E)$ after multiplying them with a large number whenever, while applying Newton's method, the recursively computed determinants become too small in magnitude. This renormalization amounts to starting the recursion with a higher value of the arbitrary constant Δ_0 (or Δ_1). More generally, other recursively connected sequences of determinants $\{\tilde{\Delta}_m(E)\}$ may be defined such that

the zeros of $\tilde{\Delta}_m(E)$ and $\Delta_m(E)$ are common but $\tilde{\Delta}_m(E)$ may be given any desired asymptotic behaviour for large m. This is done by multiplying the recursion (2.5) by a function of m say f(m). The corresponding infinite determinant $\tilde{\Delta}(E)$ and its various order truncations are related to the respective quantities for $\Delta(E)$ by the relation

$$\tilde{\Delta}_m(E) = f(m-2)\, f(m-4) \ldots f\,(0 \text{ or } 1)\;\; \Delta_m(E)\,, \quad (2.18)$$

where the rhs contains f(0) (or f(1)) for the even (or odd) eigenvalues. Clearly $\tilde{\Delta}_m(E)$ can be given any asymptotic behaviour for large m by properly choosing the function f(m). Since f(m) is independent of E by definition, the zeros of $\tilde{\Delta}_m(E)$ and $\Delta_m(E)$ are common and they are equally suited for the computation of the eigenvalues. The 'renormalization' suggested above is a special case of this multiplication in which all rows are left intact except one which is multiplied by a large number.

To see the stability of the zeros of $\Delta_m(E)$ as $m \to \infty$ we first consider the same problem for the harmonic oscillator ($H = p^2+x^2$) which is exactly soluble. In the case of the harmonic oscillator the zeros of the characteristic polynomial $\Delta_m(E)$ are real and the ratio of successive polynomials is

$$\frac{\Delta_{m+2}(E)}{\Delta_m(E)} = -\frac{(2m+1 - E)}{(m+1)(m+2)} \quad .$$

The zeros of $\Delta_{m+2}(E)$ consist of all zeros of $\Delta_m(E)$ plus a zero at $E = 2m+1$. Thus the eigenvalues resulting from the solution of $\Delta_m(E)=0$ are reproduced exactly by the solutions of $\Delta_{m+2}(E)=0$ for all m. This is characteristic of an exactly soluble problem. For the quartic anharmonic or the pure quartic oscillator the zeros of successive order polynomials are different. For a given E and sufficiently large m, however,

$$\frac{\Delta_{m+2}(E)}{\Delta_{m-4}(E)} \sim -\frac{\lambda}{m^2}, \quad m \to \infty .$$

This implies that the largest order term in the ratio of $\Delta_{m+2}(E)/\Delta_m(E)$ is independent of E for $m \to \infty$. The successive polynomials as a function of E therefore differ by a multiplicative constant (depending upon m) for large m. Hence, the zeros of $\Delta_m(E)$ stabilize for large m. The above discussion on stability follows Banerjee et al. (to be published).

II.5 Checks for the Eigenvalues

The confidence in the accuracy of the computed eigenvalues is derived from the following checks:

(i) Computations were done with several different initial estimates for each eigenvalue. The intermediate numbers involved in the computation are different for different initial estimates but the final results for the eigenvalues remain the same in all cases.

(ii) The eigenvalues were computed using several values of the scaling α in the range given by eqn. (2.10). Its effect is that the stabilization of an initial estimate for an eigenvalue to 16 figures occurs at slightly different point in recursions (2.7) and (2.8). Each $E_n(\lambda)$ obtained in this work was thus checked and confirmed by using 3 or 4 different values of α.

(iii) Three separate computations using an increasing, a decreasing and a nearly flat sequence of determinants (see section II.4) yielded the same values for $E_n(\lambda)$.

(iv) Sufficiently large order determinant Δ_M containing the appropriate scaling is evaluated for two neighbouring values of E. Opposite signs of Δ_M indicates that an eigenvalue is crossed. The computed eigenvalues are thus tested and in the process are upper and lower bounded in the last significant figure.

II.6 Eigenfunctions

When E is set equal to a computed eigenvalue in recursion (2.5) the resulting coefficients $\{a_m(E)\}$ provide a very convenient representation for the corresponding eigenfunction through the expansion (2.1). The following properties of the solutions of the Schrödinger equation $\psi(x,E)$ are important to note in this connection (Titchmarsh 1961):

(i) The eigenfunction associated with the n-th eigenvalue $\psi_n(x;E_n)$ has n zeros in the classical region and $\psi_n(x;E_n) \to 0$ as well as $\psi_n'(x;E_n) \to 0$ as $x \to \pm\infty$.

(ii) For E not exactly equal to an eigenvalue, $\psi(x;E)$ can have at most one zero in the nonclassical region on both sides of the axis and as $x \to \pm\infty$ it goes either to $+\infty$ or $-\infty$.

(iii) The blow up of $\psi(x;E)$ starts in the nonclassical region and shifts to larger $|x|$ as E approaches an eigenvalue.

(iv) As E crosses an eigenvalue, $\psi(x;E)$ changes its sign of blow up in the nonclassical region and tends to infinity with opposite sign.

The expansion coefficients $\{a_m(E)\}$ are evaluated recursively from (2.5) for various computed eigenvalues. It is observed that the sign of $\{a_m\}$ stabilizes after a certain sufficiently large index either to plus or minus sign which implies that the computed $\psi(x,E) \to +\infty$ or $-\infty$ as $x \to \pm\infty$. However, this large $|x|$ behaviour does not affect the computation of the accurate eigenfunctions significantly. Since the eigenvalues used are accurate to 15 significant figures, the computed eigenfunctions reach extremely small values in the nonclassical region before the blow up starts. The part of the computed eigenfunctions where the blow up occurs for large $|x|$ may therefore be replaced by zero without losing much information.

To test how well the computed eigenfunctions satisfy the Schrödinger equation we compare the two sides of $H\psi(x)/\psi(x) = E$ at various points x. For the first ten eigenfunctions which we have computed for $\lambda = 1$ the test equality is satisfied to 13-14 significant figures from x=0 to points well outside the classical region. For example, in the case of the 10th eigenfunction of the quartic anharmonic oscillator with $\lambda=1$, the test equality $H\psi_{10}/\psi_{10} = E_{10}$ is satisfied to at least 13 significant figures in the entire classical region ($x \lesssim E_{10}^{1/4}$). At a point $x \approx 1.5\ E_{10}^{1/4}$ the test equality is still satisfied to 10 significant figures, where the value of the computed eigenfunction $\psi_{10}\ (x = 1.5\ E_{10}^{1/4})$ is $O(10^{-16})$ relative to $\psi_{10}(x=0)=1$. The accuracy of the computed eigenfunctions are also checked by evaluating them for two neighbouring values of E which upper and lower bound the eigenvalues in the 15th significant figure. Although, the sign of the expansion coefficients $\{a_m\}$ stabilizes to all plus or all minus beyond a sufficiently high index m=M, the difference in the corresponding computed values of $\psi(x;E)$ for these neighbouring values of E is found to be less than $O(10^{-15})$ for all $|x| < x_A$, where x_A is the distance from the origin to the point in the nonclassical region at which $\psi(x;E)$ begins to increase in magnitude. Satisfying the virial theorem by the computed eigenfunctions was used in the earlier literature (e.g. Chan and Stelman 1963) to test t

accuracy. However, the fulfilment of the virial theorem is a necessary but not sufficient requirement (Löwdin 1959).

The norm of the computed eigenfunction is,

$$\int_{-\infty}^{+\infty} |\psi_n(x)|^2 \, dx = \sum_m \sum_l a_m^{(n)} a_l^{(n)} \int_{-x_A}^{+x_A} x^{m+l} e^{-2\alpha x^2} dx \ , \quad (2.19)$$

where the range of integration is truncted at x_A — the point in the nonclassical region at which the computed eigenfunction $\psi_n(x)$ begins to increase in magnitude. The value of $\psi_n(x)$ is sufficiently small for $|x| > x_A$ as discussed above and the contribution to the normalization from the rest of configuration space is estimated to be $< O(10^{-16})$. The integrals in eqn. (2.19) are obtained recursively starting from the incomplete Gaussian integral $\int_0^1 e^{-\beta x^2} dx$ (see Appendix B). The plots of some normalized computed eigenfunctions are shown in Fig. (II.1).*

II.7 Features of the Method

In this section some features of the method are seen in comparison with the other methods used for this eigenvalue problem.

(i) It may be noted that no integration or diagonalization is necessary in this method which makes it attractive for the eigenvalue problems of the linear operators.

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* The vertical lines in the figure correspond to the classical turning points.

(ii) In perturbation theory with λ as the small parameter, this problem belongs to the singular perturbation class. The uniform applicability of this method for all λ underlines its nonperturbative character.

(iii) In view of the Section II.1 an expansion for the eigen-functions like (2.1) with α = constant may be called as a 'fixed scale' expansion. Such an expansion is suitable only in a small regime of values of (n,λ) where the scale happens to be close to the appropriate value and it becomes unfavourable in the other regimes of (n,λ). The variational and most of the numerical methods applied earlier use the expansion

$$\psi_n\ (x;\lambda) \ = \ e^{-x^2/2} \sum_{m=0}^{\infty} a_m x^m \qquad (2.20)$$

in all regimes of (n,λ). This expansion has a fixed scale $\alpha = \frac{1}{2}$ and is suitable only in the 'near harmonic' regime. It is therefore not surprising that for higher n or λ $(n\lambda >> \frac{1}{8})$ the eigenvalues could not be accurately calculated in the above works.

(iv) The need for introducing a scaled basis was also realised by Reid (1970) who used the linear variation method for the pure quartic oscillator eigenvalue problem. However, in a variational framework the use of a scaled basis becomes intractably laborious for the following reasons. In a **variational** computation the first n (say) eigenvalues are

obtained together. Since the appropriate scaling is different for different n and λ a single scaling is not suitable for the computation of all n eigenvalues. A compromise scaling must therefore be used. But as n increases this compromise scaling becomes unfavourable for more and more eigenvalues. The wayout is to compute each eigenvalue separately using an appropriately scaled set of basis functions. This is intractably laborious in a variational scheme. In our method the use of an appropriately scaled basis merely requires that a proper value of the scaling α obtained from formula (2.10) be used in recursions (2.5), (2.7) and (2.8). Since each eigenvalue is computed individually there are no carry over errors.

(v) Computation with a larger basis is very simply done in this method by continuing the recursions (2.5), (2.7) and (2.8) for increasing m. In contrast a variational calculation with a larger basis requires integration and the subsequent diagonalization of a large matrix which beyond a size is intractable. For instance, the 10000th eigenvalue of the quartic anharmonic oscillator stabilizes to a 15 figure accuracy (in 3 minutes on IBM 7044) at a point in the recursions which corresponds to the use of nearly 17500 terms in the expansion (2.1). A variational calculation of this size is inconceivable.

(vi) The method of infinite determinant for the eigenvalue problems (Whittaker and Watson 1927) was used by Kerner (1951) and Biswas et al. (1973). These attempts had a limited success. The primary reason for this is the use of a 'fixed scale' expansion as discussed above. In the typical case of the quartic anharmonic oscillator (Biswas et al. 1973), only the lowest 8 eigenvalues could be obtained (using the expansion in the basis functions $\{x^m e^{-x^2/2}\}$), until the numerical errors become too severe. Besides, in this work, the procedure used for evaluating the eigenvalues consists of expanding the characteristic polynomials in powers of E and then finding its zeros. This is numerically inadvisable (see Fox and Mayers 1968) because the uncertainties in the coefficients of the polynomials are highly correlated and the expanded polynomials with rounded coefficients are badly conditioned with respect to its zeros. Biswas et al. also carried out numerical investigations on the 'amount of normalization and the extent of orthogonality' of the computed eigenfunctions in order to test their correctness. The overlap integrals required were evaluated by integration over x from $-\infty$ to $+\infty$. We have seen in Section II.6 that any solution of the Schrödinger equation $\psi(x;E) \to +\infty$ or $-\infty$ as $x \to \pm\infty$, unless E is exactly equal to an eigenvalue. Even a truncated expansion (truncated at a certain high index) gives a hump in the nonclassical region in the computed

eigenfunction, where the actual eigenfunction decays monotonically. The overlap integrals evaluated by integrating over infinite limits are therefore inaccurate and the test of the eigenfunctions used by Biswas et al. is inconclusive.

TABLE (II.1) ; Stabilization of the computed eigenvalues
(System: The Quartic Anharmonic Oscillator)

Iteration number		Numbers of $\{\Delta_m(E)\}$ required	Stabilized correction, δE	$E_{initial} + \delta E\ (m)$
n=0	λ=1	$E_{initial} = 1.5$	$\alpha = 2.0$	
1		17	-0.1121	1.387 916 248 824 27
2		[illegible]7	0.4428×10^{-2}	1.392 344 510 018 44
3		22	0.7132×10^{-5}	1.392 351 641 726 52
4		34	-0.1962×10^{-9}	1.392 351 641 530 29
5		55	0.2638×10^{-16}	1.392 351 641 530 29
n=10	λ=1000	$E_{initial}=502.9864$	$\alpha = 27.86$	
1		35	-0.1001	502.886 327 005 776
2		44	0.7228×10^{-4}	502.886 399 286 167
3		56	-0.1451×10^{-8}	502.886 399 284 716
4		68	0.5718×10^{-15}	502.886 399 284 716

TABLE (II.1)(...Contd.): Stabilization of the computed eigenvalues. (System: The Quartic Anharmonic Oscillator)

Iteration number		Numbers of $\{\Delta_m(E)\}$ required	Stabilized correction, δE	$E_{initial} + \delta E$ (m)
n=1000	λ=0.0001	$E_{initial}$ = 2134.453	α = 1.0	
1		1682	-0.2090	2 134.244 535 855 36
2		1700	-0.1986×10^{-2}	2 134.242 547 928 25
3		1725	-0.2694×10^{-5}	2 134.242 545 234 23
4		1744	-0.2018×10^{-8}	2 134.242 545 232 21
5		1764	-0.1312×10^{-11}	2 134.242 545 232 21
n=1000	λ=40000	$E_{initial}$ = 747 785.382	α = 442.83	
1		1681	0.3871×10^{-1}	747 783.421 517 234
2		1697	-0.1440×10^{-4}	747 783.421 502 836
3		1713	-0.3001×10^{-8}	747 783.421 502 834
4		1718	0.9092×10^{-10}	747 783.421 502 834

TABLE (II.2) : Comparison of our Results for E_n ($\lambda = 1$) with the Results of Earlier Calculations.

Quantum number	E_n ($\lambda = 1$) for the Quartic Anharmonic Oscillator	
n	This work	Earlier works
		1 392 35 164 ~~1.387 187 78~~ (a)
0	1.392 351 641 530 29	1.392 351 641 530 29 (b)
		1.392 350 653 679 1 (c)
10	53.449 102 139 665 3	53.448 404 6 (d)
100	1 035.544 183 138 91	1 035.544 04 (d)
1000	21 932.783 710 666 9	21 932.783 6 (d)
10000	471 103.777 790 809	471 103.778 (d)
	E_n ($\lambda = 1$) for the Pure Quartic Oscillator	
	This work	Earlier works
0	1.060 362 090 484 18	1.060 362 090 48 (e)
10	50.256 254 516 682 9	50.256 254 516 7 (e) 50.256 254 0 (d)
100	1 020.989 992 105 37	1 020.989 99 (d)
1000	21 865.262 118 137 7	21 865.262 1 (d)
10000	470 790.294 427 023	470 790.293 (d)

(a) Hioe and Montroll (1975) - Eqn. (III.9).
(b) Biswas et al. (1973).
(c) Graffi et al. (1969).
(d) Hioe and Montroll (1975) - sophisticated WKB values.
(e) Reid (1970).

TABLE (II.3) : Eigenvalues of the Pure Quartic Oscillator ($H = p^2 + \lambda x^4$) and the Quartic Anharmonic Oscillator ($H = p^2 + x^2 + \lambda x^4$) for $\lambda = 1$.

Quantum number n	Pure Quartic Oscillator Eigenvalues	Quartic Anharmonic Oscillator Eigenvalues
0	1.060 362 090 484 18	1.392 351 641 530 29
1	3.799 673 029 801 40	4.648 812 704 212 08
2	7.455 697 937 986 74	8.655 049 957 759 31
3	11.644 745 511 378 2	13.156 803 898 049 9
4	16.261 826 018 850 2	18.057 557 436 303 3
5	21.238 372 918 236 0	23.297 441 451 223 2
6	26.528 471 183 682 5	28.835 338 459 504 2
7	32.098 597 710 968 3	34.640 848 321 111 3
8	37.923 001 027 034 0	40.690 386 082 106 4
9	43.981 158 097 289 7	46.965 009 505 675 5
10	50.256 254 516 682 9	53.449 102 139 665 3
11	56.734 214 055 173 0	60.129 522 959 157 8
12	63.403 046 986 718 9	66.995 030 001 247 2
13	70.252 394 628 616 6	74.035 874 359 102 5
14	77.273 200 481 984 0	81.243 505 050 767 2
15	84.457 466 274 942 0	88.610 348 800 799 2
16	91.798 066 808 991 2	96.129 642 045 234 1
17	99.288 606 660 493 3	103.795 300 322 273
18	106.923 307 381 733	111.601 815 045 173

Table (II.3) (..Contd.)

Quantum number n	Pure Quartic Oscillator Eigenvalues	Quartic Anharmonic Oscillator Eigenvalues
19	114.696 917 384 985	119.544 170 733 050
20	122.604 639 000 999	127.617 777 795 355
21	130.642 068 748 630	135.818 417 325 610
22	138.805 147 911 395	144.142 195 296 398
23	147.090 121 257 604	152.585 504 205 574
24	155.493 502 268 682	161.144 990 694 513
25	164.012 043 622 865	169.817 528 001 595
26	172.642 711 962 845	178.600 192 366 876
27	181.382 666 185 768	187.490 242 692 950
28	190.229 238 652 463	196.485 102 910 221
29	199.179 918 833 747	205.582 346 604 423
30	208.232 339 005 144	214.779 683 549 177
31	217.384 261 674 103	224.074 947 352 600
32	226.633 568 481 138	233.466 087 479 375
33	235.978 250 361 696	242.951 154 951 147
34	245.416 398 791 936	252.528 299 061 493
35	254.946 197 970 798	262.195 757 468 520
36	264.565 917 814 499	271.951 850 050 007
37	274.273 907 658 941	281.794 972 923 820
38	284.068 590 581 401	291.723 593 051 013

TABLE (II.3) (...Contd.)

Quantum number n	Pure Quartic Oscillator Eigenvalues	Quartic Anharmonic Oscillator Eigenvalues
39	293.948 458 266 006	301.736 243 351 187
40	303.912 066 348 384	311.831 518 269 701
41	313.958 030 183 978	322.008 069 744 845
42	324.085 020 992 133	332.264 603 530 091
43	334.291 762 334 482	342.599 875 832 547
44	344.577 026 891 585	353.012 690 233 780
45	354.939 633 506 395	363.501 394 863 479
46	365.378 444 467 063	374.066 379 800 092
47	375.892 363 004 933	384.705 074 675 721
48	386.480 330 986 517	395.416 946 465 263
49	397.141 326 780 674	406.200 997 442 128
50	407.874 363 284 438	417.056 263 284 848

TABLE (II.4) : The Quartic Anharmonic Oscillator Eigenvalues for Various values of λ.

$\lambda \backslash n$	0	1	2
.00001	1.000 007 499 368 76	3.000 037 498 968 31	5.000 097 496 155 56
.0001	1.000 074 986 880 20	3.000 374 895 936 12	5.000 974 515 938 59
.001	1.000 748 692 673 19	3.003 739 748 168 73	5.009 711 872 788 11
.01	1.007 373 672 081 38	3.036 525 304 513 35	5.093 939 132 742 31
.1	1.065 285 509 543 72	3.306 872 013 152 92	5.747 959 268 833 56
1.0	1.392 351 641 530 29	4.648 812 704 212 08	8.655 049 957 759 31
10	2.449 174 072 118 39	8.599 003 454 807 77	16.635 921 492 413 8
100	4.999 417 545 137 59	17.830 192 715 952 5	34.873 984 261 994 8
1000	10.639 788 711 328 1	38.086 833 459 382 3	74.681 404 200 164 8
10000	22.861 608 870 272 5	81.903 316 953 284 5	160.685 912 611 712
40000	36.274 458 133 736 8	129.973 351 403 294	255.017 677 289 574

TABLE (II.4) (...Contd.) : The Quartic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	3	4	5
.00001	7.000 187 490 157 29	9.000 307 479 696 43	11.000 457 463 499 5
.0001	7.001 874 016 667 66	9.003 072 972 044 61	11.004 571 355 129 7
.001	7.018 652 592 057 52	9.030 549 536 074 71	11.045 390 587 179 5
.01	7.178 573 180 700 50	9.289 479 816 311 89	11.425 792 646 186 3
.1	8.352 677 825 785 75	11.098 595 622 633 0	13.969 926 197 742 8
1.0	13.156 803 898 049 9	18.057 557 436 303 3	23.297 441 451 223 2
10	25.806 276 215 055 7	35.885 171 222 253 9	46.729 080 900 817 1
100	54.385 291 571 605 1	75.877 004 028 669 7	99.032 837 315 407 5
1000	116.603 198 937 293	162.802 374 136 975	212.594 183 409 734
10000	250.950 743 891 713	350.435 896 215 566	457.654 575 005 690
40000	398.290 246 956 059	556.200 474 630 524	726.405 686 448 353

TABLE (II.4)(...Contd.) : The Quartic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	6	7	8
.00001	13.000 637 440 292 3	15.000 247 408 300 5	17.001 087 567 750 3
.0001	13.006 369 059 122 7	15.008 465 397 365 0	17.010 861 805 528 7
.001	13.065 163 577 678 5	15.085 856 587 626 0	17.107 457 792 553 5
.01	13.586 715 801 589 6	15.771 515 085 042 6	17.979 510 583 711 2
.1	16.954 794 686 144 1	20.043 863 604 188 5	23.229 552 179 939 3
1.0	28.835 338 459 504 2	34.640 848 321 111 3	40.690 386 082 106 4
10	58.241 298 739 755 2	70.351 051 939 234 7	83.005 867 037 585 3
100	123.640 697 623 378	149.545 657 443 288	176.628 655 957 714
1000	265.519 951 678 280	321.244 760 274 355	379.511 311 178 729
10000	571.647 791 619 426	691.663 457 635 372	817.156 874 968 737
40000	907.329 749 584 390	1 097.832 281 319 18	1 297.030 657 027 22

TABLE (II.4)(...Contd.) : The Quartic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	9	10
.00001	19.001 557 315 867 7	21.001 657 251 378 9
.0001	19.013 556 630 636 7	21.016 550 255 042 5
.001	19.133 955 491 852 3	21.163 358 105 705 8
.01	20.210 070 452 796 0	22.462 605 642 166 2
.1	26.505 554 752 536 6	29.866 525 234 671 3
1.0	46.965 009 505 675 5	53.449 102 139 665 3
10	96.156 262 981 197 7	109.772 570 864 335
100	204.794 774 512 945	233.966 225 876 236
1000	440.114 532 233 656	502.885 399 284 716
10000	947.685 961 666 079	1 082.883 518 002 19
40000	1 504.223 045 052 05	1 718.834 435 887 08

TABLE (II.4)(...Contd.) : The Quartic Anharmonic Oscillator Eigenvalues for Various Values of λ .

λ \ n	100	1000
.00001	201.151 292 371 240	2 015.807 858 415 28
.0001	202.494 079 859 242	2 134.242 545 232 21
.001	214.438 455 291 852	2 818.485 517 618 20
.01	285.365 070 285 076	5 019.741 907 332 61
.1	504.896 936 630 097	10 294.061 322 693 9
1.0	1 035.544 185 138 91	21 932.785 710 666 9
10	2 206.428 665 064 32	47 138.656 955 223 2
100	4 742.160 919 320 88	101 504.115 156 099
1000	10 211.359 950 956 0	218 659.377 961 231
10000	21 997.240 274 526 9	471 075.928 375 957
40000	34 917.793 493 777 1	747 783.121 502 834

TABLE (II.5) : Eigenvalues of the Quartic Anharmonic Oscillator ($H = p^2 + x^2 + \lambda x^4$) in Regimes of Extreme Values of (n, λ).

$n \backslash \lambda$	0.0001	40000
0	1.000 074 986 880 20 (near harmonic regime)	36.274 458 133 736 8 (near quartic regime)
1000	2 134.242 545 232 21 (boundary layer)	747 783.421 502 834 (near quartic/WKB regime)

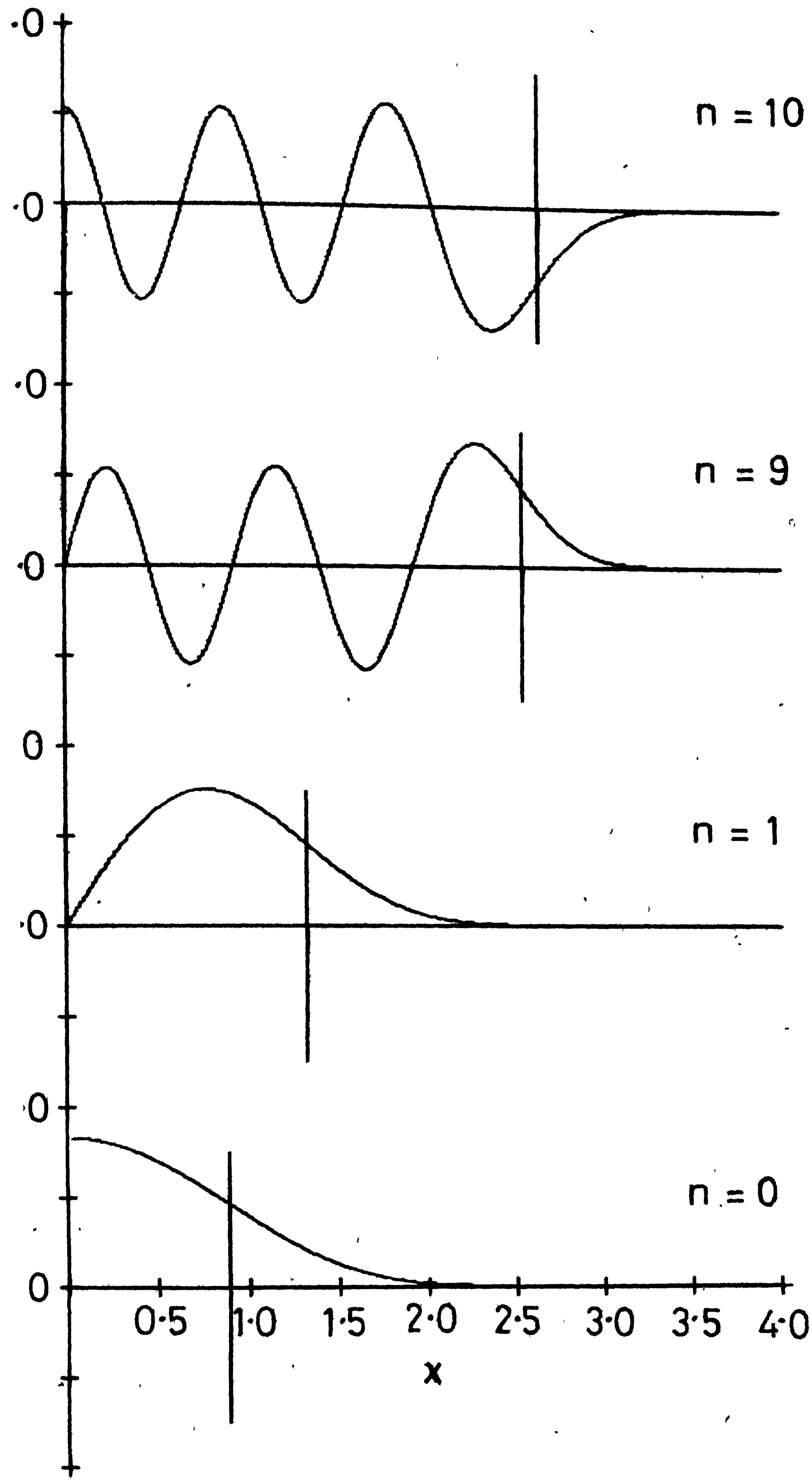

Fig. II·1 Quartic Anharmonic Oscillator Eigenfunctions for $\lambda = 1$

CHAPTER III

THE GENERAL ANHARMONIC OSCILLATOR

III 1 Introduction

The eigenvalue problem of the general anharmonic oscillator described by the Hamiltonian

$$H = p^2 + x^2 + \lambda x^{2\mu} , \qquad (3.1)$$

where $\lambda > 0$, $\mu = 3, 4, \ldots$ and $p = -i\frac{d}{dx}$, is considered in this chapter. Using the scaling arguments similar to those in Chapter I, it follows that the eigenvalues of $H(k,\lambda) = p^2 + kx^2 + \lambda x^{2\mu}$ are given by $E_n(k,\lambda) = k^{\frac{1}{2}} E_n(1, \lambda')$, where $\lambda' = k^{-3/2}\lambda$. It ensures that the eigenvalue problem of the anharmonic oscillator $H(k,\lambda)$ can be completely described in terms of the reduced Hamiltonian $H(1,\lambda)$.

A straightforward perturbative solution of this problem runs into difficulties. The perturbation expansion for the eigenvalues in powers of λ is not convergent but asymptotic (Simon 1970). The coefficients in the perturbation series grow very fast and the construction of various Padé approximants become extremely involved. The numerical results of Graffi et al. (1971) for the octic anharmonic oscillator

(μ=4 in (3.1)) suggest that Padé approximants do not converge to the exact eigenvalue. However, mixed Borel-Padé method were utilized to obtain a few eigenvalues. Non-perturbative calculations have been relatively more successful. Biswas et al. (1973) extended the 'Hill determinant' method, used for the quartic anharmonic oscillator problem, for this case. They used the basis functions $\{x^m e^{-x^2/2}\}$ for the expansion of the eigenvalues for the sextic and the octic anharmonic oscillators (μ=3 and 4 respectively in (3.1)) for values of λ in the range $0 < \lambda \leq 100$ for n=0 and $0 < \lambda \leq 10$ for n=2. However, the accuracy of the computed eigenvalues in their work reduces significantly as one goes from the quartic to the sextic or the octic anharmonic oscillator, besides, the evaluation of the eigenvalues gets confined to smaller regime of (n,λ) values. Lakshmanan and Prabhakaran (1973) obtained semiclassically an asymptotic expression for $E_n^{(2\mu)}(\lambda)$ in the μ=3 case. Truong (1975) used Weyl-quantization prescription to study the sextic anharmonic oscillator eigenvalues but no new results were obtained. For sufficiently large n, the WKB approximation method has been used to obtain approximate eigenvalues.

The most recent and extensive work on the general anharmonic oscillator eigenvalue problem is due to Hioe, MacMillen and Montroll (1976). They distinguished two limiting regimes

of values of (n,λ) for the eigenvalues $E_n^{(2\mu)}(\lambda)$ analogous to the similar distinction made for the quartic anharmonic oscillator eigenvalues. In one regime the energy eigenvalues differ slightly from the harmonic oscillator levels (the 'near harmonic' regime); in the other they differ slightly from the pure 2μ-ic oscillator eigenvalues (the 'near pure anharmonic' regime). The above two limiting regimes are separated by a regime called the 'boundary layer' in which the energy eigenvalues are not 'nearly harmonic' or 'nearly pure anharmonic'. Hioe et al. used different formulations of the eigenvalue problem in various regimes and constructed several simple formulae with different ranges of validity. Using Bargmann representation, they developed numerical algorithms from which the energy eigenvalues in the small n regime may be computed. The algorithm is similar to that developed for the quartic anharmonic oscillator eigenvalue problem. First few eigenvalues were thus computed to 5-6 significant figures for the sextic and the octic anharmonic oscillators, for various value of λ. However, the size of the determinants, required for the computation of the eigenvalues, increases rapidly with μ or n, making the evaluation of higher eigenvalues laborious.

We show in this chapter that the method described in Chapter II may be extended to solve the general anharmonic

oscillator eigenvalue problem and eigenvalues of arbitrarily high accuracy are obtainable in this case in all regimes of (n,λ) as for the quartic anharmonic oscillator problem.

III.2 The Appropriate Scaling Formula

The eigenvalues $E_n^{(2\mu)}(\lambda)$ and the eigenfunctions $\psi_n^{(2\mu)}(x;\lambda)$ of a general ahnarmonic oscillator ($H = p^2 + x^2 + \lambda x^{2\mu}$) are the solutions of the Schrödinger equation:

$$[-\frac{d^2}{dx^2} + x^2 + \lambda x^{2\mu}]\,\psi_n^{(2\mu)}(x;\lambda) = E_n^{(2\mu)}(\lambda)\,\psi_n^{(2\mu)}(x;\lambda), \tag{3.2}$$

with the boundary condition $\psi_n^{(2\mu)}(x;\lambda) \to 0$ as $x \to \pm\infty$. We write eigenfunctions in the form

$$\psi_n^{(2\mu)}(x;\lambda) = e^{-\alpha x^2} \sum_{m=0}^{\infty} a_m x^m, \tag{3.3}$$

where α is the scaling constant. A formula for determining the appropriate scaling α for any μ is obtained along the same lines as for the quartic anharmonic oscillator (section II.1). The exact n-th eigenfunction has n zeros in the region of oscillation which, for sufficiently large n, is $\sim(E_n^{(2\mu)}/\lambda)^{1/2\mu}$. In the WKB approximation

$$E_n^{(2\mu)}(\lambda) \approx C\,\lambda^{\frac{1}{\mu+1}}\,(n+\tfrac{1}{2})^{\frac{2\mu}{\mu+1}}.$$

Hence, the region of oscillation $\sim\lambda^{-\frac{1}{2(\mu+1)}}\,(n+\frac{1}{2})^{\frac{1}{(\mu+1)}}$.

For an effective expansion the region of oscillation must

include the span of first n (or a number proportional to n) basis functions. The appropriate scaling formula is thus obtained by setting the region of oscillation of the nth eigenfunction equal to the width of the nth basis function ($\sim\alpha^{-1/2}\ n^{1/2}$), which yields

$$\alpha(n,\lambda) \ \sim (n + \tfrac{1}{2})^{\frac{\mu-1}{\mu+1}} \lambda^{\frac{1}{\mu+1}} .$$

The above scaling formula is not expected to be good when n and/or λ is small, in view of the WKB approximation for $E_n^{(2\mu)}(\lambda)$ used in the derivation. However, for small n, small λ the scaling must approach 1/2 — the appropriate scaling for the harmonic oscillator. Hence, the scaling formula valid in all regimes of (n,λ) and for any μ is

$$\alpha(n,\lambda) = \tfrac{1}{2} + (n + \tfrac{1}{2})^{\frac{\mu-1}{\mu+1}} \lambda^{\frac{1}{\mu+1}} \tag{3.4}$$

The following regimes may be distinguished according to the above scaling formula:

$(n + \frac{1}{2})^{\frac{\mu-1}{\mu+1}} \lambda^{\frac{1}{\mu+1}} \ll \frac{1}{2}$ is the near harmonic regime,

$(n + \frac{1}{2})^{\frac{\mu-1}{\mu+1}} \lambda^{\frac{1}{\mu+1}} \gg \frac{1}{2}$ is the pure anharmonic regime,

$(n + \frac{1}{2})^{\frac{\mu-1}{\mu+1}} \lambda^{\frac{1}{\mu+1}} \approx \frac{1}{2}$ is the boundary layer between the above two regimes.

The value of the combination $(n + \frac{1}{2})^{\mu-1}\lambda$ determines the regime to which the eigenvalue $E_n^{(2\mu)}(\lambda)$ belongs. It may

be seen from above that the range of (n,λ) values for the 'near harmonic regime' dimnishes on increasing μ. Hence the eigenvalues of general anharmonic oscillators, obtained from the methods which use a finite term expansion for the eigenfunctions in the harmonic oscillator basis $\{x^m e^{-x^2/2}\}$, deteriorate in accuracy on going to oscillators of higher μ. The use of basis, appropriately scaled according to the regime, leads to a uniform treatment of the anharmonic oscillators eigenvalue problem for all μ and in all regime of (n,λ).

III.3 Method

The expansion (3.3) on substitution into the Schrödinger equation for the general anharmonic oscillator (3.2) yields the following $(\mu+2)$-term linear recurrence relation among the expansion coefficients $\{a_m\}$:

$$(m+1)(m+2)\ a_{m+2} + (E-4\alpha m-2\alpha)\ a_m + (4\alpha^2-1)a_{m-2} - \lambda\, a_{m-2\mu} = 0\,. \tag{3.5}$$

The even and odd parity solutions are obtained respectively by assigning the initial conditions (i) $a_0=1$, $a_1=0$ (ii) $a_0=0$, $a_1=1$. We divide the recursion (3.5) by $(m+1)(m+2)$ and rewrite it in the following notations

$$a_{m+2} + d_{m,m}\ a_m + d_{m,m-2}\ a_{m-2} + d_{m,m-2\mu}\ a_{m-2\mu} = 0\ ,$$

where

$$d_{m,m} = \frac{(E-4\alpha m-2\alpha)}{(m+1)(m+2)}, \quad d_{m,m-2} = \frac{(4\alpha^2-1)}{(m+1)(m+2)}, \tag{3.6}$$

$$d_{m,m-2\mu} = - \frac{\lambda}{(m+1)(m+2)} .$$

For self consistency the determinant

$$\Delta(E) = \begin{vmatrix} d_{00} & 1 & 0 & \cdot\cdot & & & & & & \\ d_{20} & d_{22} & 1 & 0 & \cdot\cdot & & & & & \\ 0 & d_{42} & d_{44} & 1 & 0 & \cdot\cdot & & & & \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\cdot & 0 & d_{m,m-2\mu} \cdot & 0 & d_{m,m-2} & d_{m,m} & 1 & 0 & \cdot\cdot & \\ \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot & \cdot\cdot \end{vmatrix} = 0. \tag{3.7}$$

The eigenvalues $E_n^{(2\mu)}(\lambda)$ are the roots of this transcendental equation. To obtain the roots numerically, we denote the determinant formed by omitting all rows and columns beyond $d_{m,m}$ in $\Delta(E)$ as $\Delta_{m+2}(E)$. The determinant $\Delta_{m+2}(E)$ may be expanded into determinants of lower orders. It yields the following $(\mu+2)$-term recurrence relation among $\{\Delta_m(E)\}$:

$$\Delta_{m+2}(E) - d_{m,m}(E)\,\Delta_m(E) + d_{m,m-2}\,\Delta_{m-2}(E)$$
$$+(-1)^{\mu-1}\, d_{m,m-2\mu}\,\Delta_{m-2\mu}(E) = 0 . \tag{3.8}$$

Hence the values of the determinants $\Delta_{m+2}(E)$ upto any order

may be determined successively in terms of Δ_0 (or Δ_1) with the help of the above recursion. The corresponding zeros of $\Delta_m(E)$, $\Delta_{m+2}(E)$,.... stabilize to an eigenvalue for large m provided the scaling α is appropriate. The procedure for the actual numerical evaluation of the eigenvalues is the same as is described in section (II.2). The Newton's method, which is used for obtaining the roots of $\Delta_m(E)=0$, requires the value of the derivative $\Delta'_m(E)$ also. The derivatives $\Delta'_m(E)$ can also be evaluated recursively with the help of the recursion :

$$\Delta'_{m+2}(E) - d'_{m,m}\,\Delta_m(E) - d_{m,m}(E)\,\Delta'_m(E) + d_{m,m-2}\,\Delta'_{m-2}(E)$$

$$+ (-1)^{\mu-1}\,d_{m,m-2\mu}\,\Delta'_{m-2\mu}(E) = 0, \qquad (3.9)$$

obtained by differentiating (3.8) with respect to E. The recursions (3.8) and (3.9) are continued on computer until the corrections for the required root of $\{\Delta_m(E)\}$ for sufficiently large m stabilize to a prescribed extent. The eigenvalues accurate to 15 significant figures may thus be computed in only 4 or 5 iterations starting from rather crude initial estimates. The initial estimates for eigenvalues for large n (and not too low λ) are obtained from the corresponding WKB approximation formulae and for low n they are obtained by evaluating a sufficiently large order determinant $\Delta_m(E)$ from recursion (3.8) at various E points.

For obtaining eigenfunctions, E is set equal to the computed eigenvalues in the recursion (3.5) and the expansion coefficients $\{a_m(E)\}$ are evaluated successively. The resulting coefficients $\{a_m(E)\}$ provide a convenient representation for the corresponding eigenfunction through the expansion (3.3). The asymptotic behaviour of the solution of the Schrödinger equation (3.2) $\sim \exp(\pm|x|^{\mu+1}/\mu+1)$, which requires

$$a_{m+2}/a_{m-2\mu} \sim \lambda/m^2, \quad m \to \infty \quad , \qquad (3.10)$$

for the coefficients in the series solution (3.3). It is seen during the computation of $\{a_m(E)\}$ that the above asymptotic dependence is satisfied actually, which ensures a decreasing (in magnitude) set of coefficients for sufficiently large m. It is now possible to obtain accurate eigenvalues and eigenfunctions for the general anharmonic oscillators for any value (n, λ).

III.4 Eigenvalues

We have obtained the eigenvalues of the sextic ($H = p^2 + x^2 + \lambda x^6$, $\lambda > 0$) and the octic ($H = p^2 + x^2 + \lambda x^8$, $\lambda > 0$) anharmonic oscillators for various values of n and λ. The eigenvalues are computed using values of α in the range:

$$\alpha(n,\lambda) = \tfrac{1}{2} + (1.5 \text{ to } 2.0)\,(n+\tfrac{1}{2})^{1/2}\;\lambda^{1/4}\text{, (for the sextic anharmonic oscillator),} \tag{3.10a}$$

$$\alpha(n,\lambda) = \tfrac{1}{2} + (2.5 \text{ to } 3.0)(n+\tfrac{1}{2})^{3/5}\;\lambda^{1/5}\text{, (for the octic anharmonic oscillator).} \tag{3.10b}$$

The range of α given above works for any value of (n,λ). The eigenvalues, thus computed, are presented in Tables (III.1) and (III.2) for n = 0, 1, 2, .. 10, 100 and 1000 and for different values of λ in the range $.00001 \leq \lambda \leq 40000$. They are evaluated to 16 figures and then are rounded off to 15 figures for the Tables. The Tables (III.1) and (III.2) include values of $E_n^{(2\mu)}(\lambda)$ for the (high n, low λ) region on the boundary layer. The computation of the eigenvalues in this region is found to be the most difficult in the earlier literature. Further, the values of $E_n^{(2\mu)}(\lambda)$ for the sextic and the octic anharmonic oscillators to this accuracy in all regimes of (n,λ) are reported here for the first time. The existing most extensive tables for $E_n^{(2\mu)}(\lambda)$, μ = 3, 4, are due to Hioe et al. (1976) who have presented the values of first six eigenvalues to 6 significant figures for the sextic anharmonic oscillator and of first four eigenvalues to 5 significant figures for the octic anharmonic oscillator. The possibility of treating all higher order general anharmonic oscillators eigenvalue problem by the same technique for any value of (n,λ) is thus established in this chapter.

TABLE (III.1) : The Sextic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	0	1	2
.00001	1.000 018 747 270 74	3.000 131 213 195 10	5.000 468 519 726 98
.0001	1.000 187 228 155 68	3.001 308 343 629 60	5.004 664 711 299 98
.001	1.001 848 815 572 51	3.012 780 960 690 10	5.044 799 925 784 58
.01	1.016 741 363 754 73	3.107 979 912 744 58	5.347 420 351 008 54
.1	1.109 087 078 465 58	3.596 036 921 220 46	6.644 391 708 656 61
1.0	1.435 624 619 003 39	5.033 395 937 720 27	9.966 621 999 718 11
10	2.205 723 269 595 63	8.114 843 118 819 54	16.641 218 108 251 1
100	3.716 974 729 208 62	13.946 206 622 895 4	28.977 295 817 634 0
1000	6.492 350 132 329 67	24.525 316 086 919 2	51.182 480 106 505 7
10000	11.478 798 042 264 5	43.457 784 742 680 4	90.821 278 911 708 8
40000	16.211 718 254 749 2	61.407 828 604 359 5	128.376 742 015 189

TABLE (III.1)(...Contd.) : The Sextic Anharmonic Oscillator Eigenvalues for Various Values of λ .

λ \ n	3	4	5
.00001	7.001 100 315 736 41	9.002 415 883 909 08	11.004 325 996 047 8
.0001	7.011 720 523 720 43	9.025 907 201 408 30	11.042 608 787 834 1
.001	7.110 092 855 860 92	9.218 581 748 732 25	11.377 008 617 207 5
.01	7.777 697 466 537 50	10.408 337 508 093 5	13.235 278 161 874 1
.1	10.237 973 721 423 9	14.307 040 046 120 [illegible]	18.801 758 333 358 2
1.0	15.989 440 787 825 7	22.910 180 430 728 6	30.622 590 570 533 3
10	27.155 085 604 651 4	39.289 330 657 370 3	52.849 512 678 258 2
100	47.564 984 581 593 5	69.046 576 526 034 7	93.073 891 695 377 6
1000	84.175 583 775 589 6	122.321 705 320 204	165.000 436 566 548
10000	149.457 970 316 356	217.261 999 779 375	293.129 422 079 698
40000	211.290 344 511 508	307.169 772 116 721	414.453 587 749 840

TABLE (III.1) (...Contd.) : The Sextic Anharmonic Oscillator Eigenvalues for Various Values of λ .

λ \ n	6	7	8
.00001	13.007 052 770 769 2	15.010 749 535 371 3	17.015 560 678 996 6
.0001	13.069 151 975 425 9	15.104 797 508 119 9	17.150 733 580 940 5
.001	13.593 156 248 671 1	15.868 288 655 234 6	18.205 461 089 989 1
.01	16.250 553 042 693 7	19.445 622 881 748 1	22.012 380 711 280 0
.1	23.685 275 396 988 3	28.928 937 081 664 6	34.509 374 585 792 2
1.0	39.051 906 854 386 1	48.141 505 571 449 5	57.845 728 456 325 1
10	67.698 071 647 819 2	83.730 950 282 579 2	100.865 986 116 256
100	119.399 778 936 835	147.837 547 351 690	178.239 969 897 024
1000	211.770 856 103 435	262.300 055 623 661	316.325 599 139 895
10000	376.275 359 274 236	466.107 291 369 825	562.158 183 022 017
40000	532.031 545 974 230	659.065 528 349 994	794.894 952 499 649

TABLE (III.1) (...Contd.) : The Sextic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	9	10
.00001	19.021 571 539 128 1	21.029 108 252 213 6
.0001	19.203 071 259 196 7	21.277 841 679 537 8
.001	20.505 977 378 524 0	23.070 422 451 241 3
.01	26.345 413 025 650 0	30.032 020 218 937 3
.1	40.408 244 096 093 5	46.508 420 818 435 4
1.0	68.128 291 836 137 7	78.958 068 575 484 3
10	119.036 133 924 034	138.185 513 922 455
100	210.437 018 157 389	244.478 367 577 563
1000	373.633 593 406 131	434.045 298 101 346
10000	664.047 420 116 392	771.456 964 189 455
40000	938.981 406 361 506	1 090.875 114 099 14

TABLE (III.1)(...Contd.): The Sextic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	100	1000
.00001	219.427 154 170 404	4 546.579 920 005 61
.0001	283.323 091 569 378	7 546.838 298 698 15
.001	437.466 348 857 205	12 847.726 240 655 2
.01	739.571 894 340 342	22 724.511 918 215 2
.1	1 295.415 788 522 79	40 541 683 937 757 5
1.0	2 287.793 556 442 03	71 700.060 494 015 6
10	4 061.435 921 466 71	127 480.962 682 801
100	7 212.486 617 611 01	226 684.523 808 084
1000	12 834.503 564 168 7	403 101.534 044 585
10000	22 821.749 928 826 2	716 823.285 169 907
40000	32 274.426 851 821 8	1 013 739.945 172 62

TABLE (III.2) : The Octic Anharmonic Oscillator Eigenvalues for Various Values of λ.

$\lambda \backslash n$	0	1	2
.00001	1.000 065 520 277 17	3.000 583 559 705 71	5.002 673 189 188 66
.0001	1.000 646 339 374 07	3.005 725 955 351 21	5.025 394 969 087 81
.001	1.005 857 514 124 73	3.047 977 747 263 14	5.190 981 366 774 52
.01	1.039 496 778 865 76	3.268 551 508 038 16	5.886 448 512 835 72
.1	1.168 970 453 245 99	3.939 721 361 041 99	7.639 948 490 635 78
1.0	1.491 019 895 362 21	5.368 778 061 748 15	10.993 737 335 505 0
10	2.114 544 621 942 13	7.929 683 082 350 76	16.711 022 381 994 9
100	3.188 654 346 492 27	12.195 021 933 630 2	26.035 458 321 253 1
1000	4.949 487 440 032 74	19.090 814 267 022 6	40.974 799 857 386 5
10000	7.778 272 214 511 10	30.106 900 557 858 1	64.760 471 754 927 2
40000	10.238 868 235 479 1	39.670 505 945 098 3	85.384 995 315 355 1

TABLE (III.2) (...Contd.) : The Octic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	3	4	5
.00001	7.008 366 684 173 81	9.020 533 490 764 59	11.[illegible]3 322 812 186 7
.0001	7.076 568 972 602 77	9.180 256 740 106 91	11.356 154 415 293 5
.001	7.507 661 558 294 58	10.045 355 306 963 2	12.821 559 688 194 8
.01	8.995 834 368 107 60	12.594 709 515 209 4	16.650 618 992 637 8
.1	12.281 167 732 276 1	17.761 215 567 788 7	23.997 086 021 463 5
1.0	18.191 100 018 514 9	26.743 448 558 041 2	36.509 236 308 241 3
10	28.022 750 232 932 1	41.494 702 572 696 9	56.898 990 129 970 3
100	43.902 113 335 199 5	65.201 815 832 253 8	89.569 748 769 825 3
1000	69.257 537 833 103 0	102.982 586 803 735	141.574 025 285 519
10000	109.562 182 579 437	162.992 157 936 368	224.137 086 582 704
40000	144.492 517 309 256	214.986 131 730 873	295.630 523 015 270

TABLE (III.2)(...Contd.) : The Octic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	6	7	8
.00001	15.080 773 250 261 9	15.157 771 938 185 9	17.219 185 575 051 6
.0001	13.620 497 420 369 9	15.984 519 524 996 2	18.455 098 918 205 9
.001	15.836 253 113 142 6	19.084 419 253 066 1	22.558 588 757 649 3
.01	21.135 638 499 788 9	26.019 385 438 593 8	31.287 657 941 939 9
.1	30.931 097 089 331 5	38.519 256 956 771 0	46.726 089 972 425 5
1.0	47.393 379 092 009 1	59.323 544 225 652 5	72.241 657 072 499 5
10	74.083 047 442 977 1	92.930 664 512 525 0	113.348 652 162 102
100	116.762 998 351 560	146.596 403 041 015	178.921 526 920 463
1000	184.646 163 268 619	231.904 927 760 861	283.114 615 544 210
10000	292.385 266 491 847	367.270 224 518 525	448.418 117 629 494
40000	385.708 384 553 478	484.514 056 324 413	591.584 145 926 580

TABLE (III.2)(...Contd) : The Octic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	9	10
.00001	19.529 739 585 535 1	21.475 815 823 094 1
.0001	21.035 900 498 433 8	23.728 451 754 605 2
.001	26.251 386 225 766 0	30.155 815 137 584 6
.01	36.921 273 635 926 1	42.905 532 936 [illegible] 2
.1	55.522 079 758 670 0	64.882 127 909 955 0
1.0	86.099 541 860 127 4	100.856 494 455 769
10	135.259 874 580 136	158.599 178 256 695
100	213.615 701 995 838	250.575 191 397 872
1000	338.080 489 508 001	396.637 899 756 015
10000	535.520 106 326 378	628.315 087 274 892
40000	706.511 061 163 711	828.950 218 446 123

TABLE (III.2)(...Contd.): The Cubic Anharmonic Oscillator Eigenvalues for Various Values of λ.

λ \ n	100	1000
.00001	401.157 029 304 53[illegible]	14 666.172 316 057 4
.0001	605.179 115 567 711	2[illegible] 107.125 099 329 9
.001	939.755 921 528 166	56 568.70[illegible] 732 732 8
.01	1 477.162 840 775 50	58 035.239 276 949 8
.1	2 333.412 136 221 38	92 039.504 286 653 5
1.0	3 693.328 703 597 06	145 860.545 560 689
10	5 850.452 007 751 74	231 165.663 873 444
100	9 270.398 457 270 35	356 368 041 845 052
1000	14 691.365 375 930 8	580 651.093 538 398
10000	23 283.471 395 490 2	920 268.033 625 388
40000	30 722.437 320 580 8	1 214 300.229 845 36

CHAPTER IV

THE DOUBLE MINIMUM OSCILLATOR

IV.1 Introduction

We consider in this chapter the eigenvalue problem of the double minimum oscillator (d.m.o.) desc.ibed by the Hamiltonian

$$H(1,\lambda) = p^2 - x^2 + \lambda x^4 , \quad \lambda > 0 . \qquad (4.1)$$

The potential function of a d.m.o. has two symmetric potential wells separated by a barrier. A feature of its eigenvalue problem is the bunching of the lower eigenvalues in pairs for sufficiently large separation between the two wells. The d.m.o. models some interesting physical problems. The vibrational spectra of some molecules possess two parallel type nearly superimposed bands, a phenomenon which may be directly related to the eigenvalue spectrum of the d.m.o. The commonly known example in this regard is the inversion spectra of the ammonia molecule (see Dennison and Uhlenbeck 1932). Besides, the potential functions of several hydrogen bonded solids are found to possess two minima in the region available for protonic movement (see Synder and Ibers 1962,

Somorjai and Hornig 1962). The most recent appearance of this model is in the spontaneous symmetry breaking (Polyakov 1977).

The computation of the splitting between the eigenvalues forming pairs has been the subject of considerable interest. The splitting depends in general on the separation between the two wells and the nature of barrier between them. The d.m.o. with potential function $V(x) = \frac{1}{2}k\ (|x| - a)^2$ is exactly solvable (Merzbacher 1961) and an expression for the splitting between the two lowest eigenvalues is $\Delta E \sim k^2 a\ \exp\ (-ka^2)$. Dennison and Uhlenbeck (1932) obtained the splitting in the WKB approximation and then compared the WKB values with the exact values for a d.m.o with potential function formed by joining two equal parabolae with a straight line. The WKB values for the splitting are found fairly accurate for large separations between the two parabolae. It is interesting to note that the WKB approximation is applied here for low n. The usefulness of these results is, however, limited to some extent, as the potential functions used in these works are non-analytic. Harmony (1971) treated the d.m.o. problem via a harmonic oscillator approximation and obtained zero-order and first-order expressions for the splitting.

The perturbation expansion of the energy eigenvalues of the d.m.o. described by (4.1) in power series of λ is

non-convergent (Simon 1970). Somorjai and Hornig (1962) obtained numerically a few energy eigenvalues (to 3-5 significant figures) for the d.m.o. with Hamiltonian $H(k,\lambda) = p^2 - kx^2 + \lambda x^4$ for five different pairs of values of (k,λ). The calculations were done by expanding the eigenfunctions in the harmonic oscillator basis functions and diagonalizing the secular determinant formed. We obtain, in this chapter, accurate eigenvalues and eigenfunctions of (4.1) using the method described in Chapter II. A WKB expression for the splitting is also obtained for this problem and the WKB values are compared with the corresponding accurate values for the splitting for various values of λ.

IV.2 Eigenvalues

The Schrödinger equation for the d.m.o. (4.1) is

$$\left[-\frac{d^2}{dx^2} - x^2 + \lambda x^4\right] \psi_n(x;\lambda) = E_n(\lambda)\, \psi_n(x;\lambda) \,. \qquad (4.2)$$

The eigenfunctions are expanded as

$$\psi(x;\lambda) = e^{-\alpha x^2} \sum_{m=0}^{\infty} a_m x^m \,, \qquad (4.3)$$

which on substitution into (4.2) yields the following 4-term recurrence relation,

$$a_{m+2} + d_{m,m}a_m + d_{m,m-2}\, a_{m-2} + d_{m,m-4}\, a_{m-4} = 0, \qquad (4.4)$$

where

$$d_{m,m} = \frac{(E - 4\alpha m - 2\alpha)}{(m+1)(m+2)}, \quad d_{m,m-2} = \frac{4\alpha^2 + 1}{(m+1)(m+2)},$$

$$d_{m,m-4} = - \frac{\lambda}{(m+1)(m+2)} .$$

The method of computing the eigenvalues from a recursion of the type (4.4) has been described in Chapter II. Therefore, the eigenvalues of the d.m.o. are obtainable with uniform accuracy in all regimes of (n,λ). The characteristic bunching of the eigenvalues in pairs occurs for small n and for sufficiently large separation between the two wells. Since the separation between the two wells $\sim\sqrt{(1/\lambda)}$, the region of interest for the present problem is the (low n, low λ) regime. For (high n, high λ) regime the eigenvalues are near pure quartic. We have therefore computed the eigenvalues in the (low n, low λ) regime and the results are presented in Table (IV.1) for the first eight eigenvalues for values of λ in the range $0.01 \leq \lambda \leq 0.20$. The values of the scaling α used in these computations lie between 0.5 and 1.0. The eigenvalues presented in the Table (IV.1) are with respect to the bottom of the potential wells at zero energy and is related to $E_n(\lambda)$ by

$$\varepsilon_n(\lambda) = \frac{1}{4\lambda} + E_n(\lambda), \qquad (4.5)$$

where $1/4\lambda$ is the depth of the potential well. The numbers $\varepsilon_n(\lambda)$ are positive definite and provide a direct look at the variation of the eigenvalues with λ. For $\lambda \to 0$, the separation between the two wells increases and the probability of penetration through the barrier approaches zero. The eigenvalues ε_{2n} and ε_{2n+1}, therefore, become nearly doubly degenerate for small n. For instance, ε_{2n} and ε_{2n+1} $(n = 0,1,2)$ are found close to each other to at least 14 significant figures for $\lambda = 0.01$. The expansion of the potential function of the d.m.o. about the minima of the well $\sim 2x^2$, for $\lambda \to 0$; therefore the lower eigenvalues $\sim\sqrt{2}(2n+1)$. The numerical results confirm this observation.

The eigenvalues of $H(k,\lambda) = p^2 - kx^2 + \lambda x^4$ are obtainable from the eigenvalues of $H(1, \lambda')$ using the scaling relation

$$E_n(k,\lambda) = k^{1/2} E_n(1, \lambda'),$$

where $\lambda' = k^{-3/2}\lambda$.

IV.3 The WKB Formula for Splitting

The splitting between the pairs of lower eigenvalues of a symmetric d.m.o. in the WKB approximation is given by (Landau and Lifshitz 1965)

$$\Delta E^{WKB} = \frac{\omega}{\pi} \exp\left[- \int_{-x_0}^{x_0} |p|\, dx\right], \qquad (4.6)$$

where $\omega^{-1} = \frac{1}{2\pi} \int_{x_0}^{x_1} p^{-1}\, dx$ and $\pm x_0$, $\pm x_1$ are the four turning

points. The derivation of the above formula assumes small probability of penetration through the barrier. For the d.m.o. described by (4.1) the turning points are given by

$$x_0^2 = \frac{1}{2\lambda}(1-u), \quad x_1^2 = \frac{1}{2\lambda}(1+u), \tag{4.7}$$

where $u = \sqrt{(4\lambda\varepsilon_n^o)}$, $\varepsilon_n^o = \frac{1}{4\lambda} + E_n^o$, E_n^o is the mean energy of the two eigenvalues forming a pair. The integrals involved in (4.6) may be expressed in terms of the complete elliptic integrals K(k) and E(k) of the first and the second kinds respectively (Gradshteyn and Ryzhik 1965)

$$\int_{-x_0}^{+x_0} |p|dx = \lambda^{1/2} \int_{-x_0}^{+x_0} [(x_0^2 - x^2)(x_1^2 - x^2)]^{1/2} dx$$

$$= 2\lambda^{1/2} \frac{x_1}{3}[(x_0^2+x_1^2) E(t) - (x_1^2-x_0^2) K(t)] \tag{4.8a}$$

and

$$\int_{x_0}^{x_1} p^{-1} dx = \frac{1}{\lambda^{1/2}} \int_{x_0}^{x_1} [(x^2-x_0^2)(x_1^2-x^2)]^{-1/2} dx$$

$$= \frac{1}{\lambda^{1/2}x_1} K(q) , \tag{4.8b}$$

where $t = (\frac{1-u}{1+u})^{1/2}$, $q = (\frac{2u}{1+u})^{1/2}$. Thus,

$$\Delta E^{WKB} = \frac{2^{1/2}(1+u)^{1/2}}{K(q)} \exp\left[-\frac{2^{1/2}}{3\lambda}(1+u)^{1/2}\{E(t) - uK(t)\}\right] \tag{4.9}$$

The values of the splitting ΔE are calculated from the above formula for various values of λ for the lowest two eigenvalues

and are compared with the corresponding accurate values in Table (IV.2). The mean energy E_n^o required in (4.9) is evaluated from Table (IV.1). The WKB values for splitting are surprisingly good.

For small λ a simple analytic approximate expression for ΔE may now be obtained from (4.9) using the following expansions for the elliptic integrals (Gradshteyn and Ryzhik 1965):

$$K(k) = \frac{\pi}{2}\left(1 + \frac{1}{4}k^2\right) + O(k^4),$$

$$E(k) = \frac{\pi}{2}\left(1 - \frac{1}{4}k^2\right) + O(k^4), \quad k \to 0 \qquad (4.10)$$

and

$$K(k) = \ln\frac{4}{k'} + \frac{1}{4}\left(\ln\frac{4}{k'} - 1\right)k'^2 + O(k'^4 \ln k'),$$

$$E(k) = 1 + \frac{1}{2}\left(\ln\frac{4}{k'} - \frac{1}{2}\right)k'^2 + O(k'^4 \ln k'),$$

$$k' = \sqrt{(1-k^2)}, \quad k \to 1, \quad k' \to 0 . \qquad (4.11)$$

On substituting these expansions in (4.9), we obtain for $\lambda\varepsilon_n^o \to 0$,

$$\Delta E^{WKB} \simeq \frac{2\sqrt{2}}{\pi}\left(1 + O(\lambda\varepsilon_n^o)\right)\exp\left[-\frac{\sqrt{2}}{3\lambda}\left(1 + O(\lambda\varepsilon_n^o \ln \lambda\varepsilon_n^o)\right)\right] . \qquad (4.12)$$

TABLE (IV.1) : The double minimum oscillator eigenvalues for various values of λ. The values tabulated are $\varepsilon_n(\lambda) = E_n(\lambda) + \frac{1}{4\lambda}$, where $E_n(\lambda)$ are the eigenvalues of $H(1,\lambda)$.

$n \backslash \lambda$	.01	.02	.05
0	1.404 043 605 297 7	1.393 527 585 044 2	1.382 301 444 053 76
1	1.404 043 605 297 7	1.393 527 587 151 0	1.382 605 783 851 38
2	4.170 193 605 999 3	4.092 029 112 820 5	4.006 049 199 465 72
3	4.170 193 605 999 3	4.092 028 608 428 7	4.006 655 436 749 52
4	6.870 088 855 714 0	6.640 484 633 304 1	5.347 173 384 952 61
5	6.870 088 855 714 0	6 640 533 622 317 3	6 576 869 564 055 15
6	9.498 578 387 197 8	9.003 118 554 271 2	8.102 324 720 641 12
7	9.498 578 387 191 1	9.005 076 381 102 1	8 514 357 705 634 85

TABLE (IV.1)(...Contd.)· The double minimum oscillator eigenvalues for various values of λ.

$n \backslash \lambda$	.04	.05	.06
0	1.371 122 236 557 54	1.358 422 105 747 79	1.345 027 201 590 10
1	1.371 308 461 512 93	1.360 133 597 773 29	1.350 326 987 540 87
2	3.991 359 951 815 14	3.746 917 080 727 93	3.542 342 543 859 88
3	3.918 263 537 997 13	3.848 838 300 057 53	3.819 606 255 058 87
4	5.838 911 090 504 90	5.369 059 360 284 71	5.181 424 577 100 94
5	6.183 906 203 843 25	6.177 383 138 505 23	6.315 544 235 545 90
6	7.424 089 289 557 84	7.470 119 938 266 43	7.750 946 881 292 35
7	8.509 274 035 240 73	8.849 281 200 220 76	9.317 731 706 581 10

TABLE (IV.1) (...Contd.): The double minimum oscillator eigenvalues for various values of λ.

n \ λ	.07	.08	.09
0	1.323 374 074 208 55	1.298 249 887 534 36	1.268 237 584 205 14
1	1.342 3[illegible]5 616 287 37	1.340 294 971 351 90	1.341 520 024 457 36
2	3.342 216 720 258 67	3.184 662 443 124 35	3.075 954 565 741 08
3	3.855 129 937 607 88	3.881 190 140 000 98	3.954 001 892 576 04
4	5.187 369 933 494 84	5.288 919 012 089 50	5.435 992 042 717 06
5	6 472 594 860 402 36	5.787 428 109 927 17	7.059 115 211 828 71
6	8.107 405 157 792 95	8.488 978 765 420 45	8.875 201 968 171 05
7	9.826 274 415 911 45	10.340 161 915 554 6	10.844 973 404 181 0

TABLE (IV.1)(...Contd.): The double minimum oscillator eigenvalues for various values of λ.

$n \backslash \lambda$	.10	.15	.20
0	1.234 507 162 786 00	1.052 499 247 956 49	0.941 750 342 076 86
1	1.546 940 363 922 54	1.421 086 890 559 30	1.535 530 204 065 82
2	3.009 498 545 456 20	3.053 667 276 570 65	3.270 577 201 715 50
3	4.043 546 019 767 00	4.589 838 495 545 43	5.148 274 740 096 02
4	5.605 133 796 683 15	6.516 658 311 767 64	7.367 134 678 671 73
5	7.336 113 319 004 21	8.664 042 111 907 84	9.827 517 529 906 06
6	9.256 031 577 195 00	11.008 958 005 345 1	12.497 859 524 783 5
7	11.334 728 355 395 9	13.526 058 520 997 8	15.553 312 548 653 9

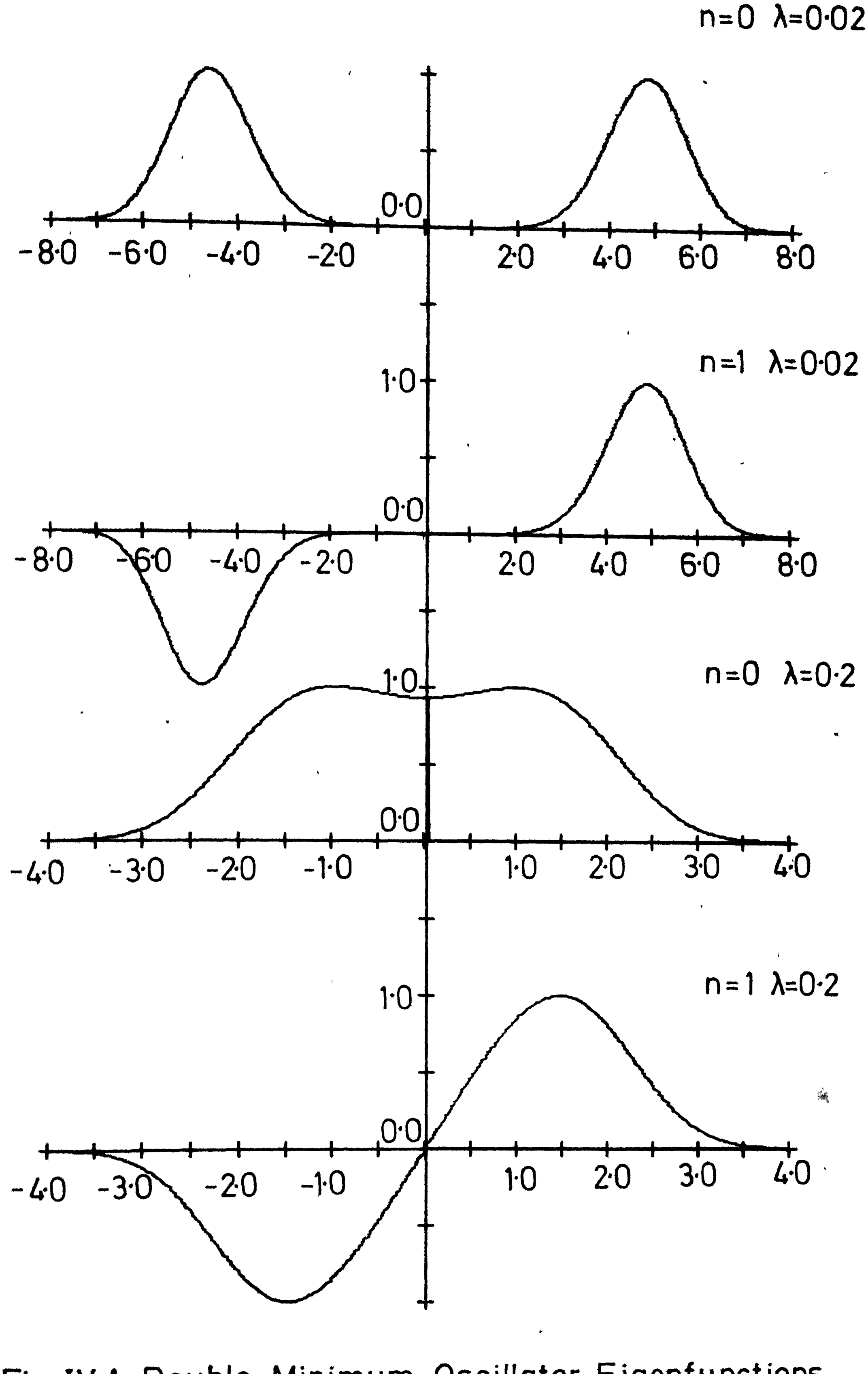

Fig. IV·1 Double Minimum Oscillator Eigenfunctions

TABLE (IV.2) : Comparison of the WKB values for the splitting with the corresponding accurate values

λ	$\Delta E_{0,1}^{\text{accurate}\dagger}$	$\Delta E_{0,1}^{\text{accurate}}/\Delta E_{0,1}^{\text{WKB}}$
.02	0.000 000 002 107 2	1.080
.03	0.000 004 339 777 6	1.082
.04	0.000 186 225 055 5	1.083
.05	0.001 711 494 025 5	1.084
.06	0.007 299 775 950 8	1.084
.07	0.020 091 542 078 8	1.082
.08	0.042 045 083 827 6	1.077
.09	0.073 282 440 234 2	1.069
.10	0.112 433 706 136 5	1.048
.11	0.157 407 347 591 1	1.048
.12	0.206 073 033 949 6	1.035
.13	0.256 643 277 892 3	1.022
.14	0.307 785 906 563 0	1.012
.15	0.358 587 642 582 8	1.004
.16	0.408 462 474 699 9	1.003
.17	0.457 059 973 642 5	1.010

$\dagger$ $\Delta E_{0,1} = E_1(\lambda) - E_0(\lambda)$.

CHAPTER V

THE TRANSITION MOMENTS

The transition moments between the anharmonic oscillator energy eigenstates $|n\rangle$ and $|n'\rangle$ are the matrix elements $\langle n|x^k|n'\rangle$. The best known estimates (Chan and Stelman 1963, Reid 1970) of the transition moments were obtained for the pure quartic oscillator using variational eigenfunctions. The variational eigenfunctions are known to be much less accurate than the corresponding eigenvalues and are unsuitable for the computation of the transition moments of high accuracy. The accurate evaluation of the eigenvalues and the eigenfunctions in this work makes it possible to obtain accurate transition moments. Further, the matrix elements $\langle n|x^k|n'\rangle$ satisfy an exact linear recurrence relation in the index k (Banerjee 1977). The recurrence relation makes possible the evaluation of all higher moments in terms of lower moments and eigenvalues, without integration.

V.1 The Recurrence Relation in $\langle n|x^k|n'\rangle$

We consider the class of Hamiltonians $H = p^2 + V(x)$, where $V(x)$ is a real polynomial function and $H|n\rangle = E_n|n\rangle$. Then

$$\langle n|[H,W]|n'\rangle = (E_n - E_{n'})\langle n|W|n'\rangle \qquad (5.1)$$

for an arbitrary operator W. On setting $W = x^k$ and $x^{k-1}p$ successively in (5.1) and using the Schrödinger equation, following relations are obtained:

$$(E_n - E_{n'}) \langle n|x^k|n'\rangle = -k(k-1)\langle n|x^{k-2}|n'\rangle - 2ik\langle n|x^{k-1}p|n'\rangle. \tag{5.2}$$

$$\begin{aligned}(E_n - E_{n'}) \langle n|x^{k-1}p|n'\rangle &= -(k-1)(k-2)\ \langle n|x^{k-3}p|n'\rangle \\ &\quad - 2i(k-1)\ E_n\ \langle n|x^{k-2}|n'\rangle \\ &\quad + 2i(k-1)\ \langle n|x^{k-2}V(x)|n'\rangle + i\langle n|x^{k-1}V'(x)|n'\rangle,\end{aligned}$$

where $V'(x) = \partial V(x)/\partial x$. (5.3)

Eliminating the matrix elements of $x^{k-1}p$ and $x^{k-3}p$ from the above two relations, we obtain

$$\begin{aligned}4k(k-1)\langle n|x^{k-2}V|n'\rangle + 2k\langle n|x^{k-1}\ V'|n'\rangle \\ = (E_n-E_{n'})^2\ \langle n|x^k|n'\rangle + 2k(k-1)(E_n+E_{n'})\ \langle n|x^{k-2}|n'\rangle \\ + k(k-1)(k-2)(k-3)\ \langle n|x^{k-4}|n'\rangle .\end{aligned} \tag{5.4}$$

For a polynomial potential $V(x)$, the equation (5.4) reduces to the required recurrence relation. The number of initial matrix elements required to start the recursion is μ for a polynomial potential $V(x)$ of degree 2μ. The recursion involves the same elements of all the matrices. Thus the nn'-th

element of the lowest μ matrices and the two eigenvalues E_n and $E_{n'}$ are sufficient to determine the nn'-th element of x^k for any k. It may be noted that without the above recursion one needs all the matrix elements of the matrix x to determine a single element of x^k. In the case of the quartic anharmonic (potential function $V(x) = x^2 + \lambda x^4$) and the pure quartic oscillator ($V(x) = \lambda x^4$) the relation (5.4) yields the following recurrence relations respectively:

$$4k(k+1)\lambda \langle n|x^{k+2}|n'\rangle = [(E_n-E_{n'})^2 - 4k^2] \langle n|x^k|n'\rangle + 2k(k-1)(E_n+E_{n'}) \langle n|x^{k-2}|n'\rangle + k(k-1)(k-2)(k-3) \langle n|x^{k-4}|n'\rangle , \qquad (5.5)$$

and

$$4k(k+1)\lambda \langle n|x^{k+2}|n'\rangle = (E_n-E_{n'})^2 \langle n|x^{k\cancel{+2}}|n'\rangle + 2k(k-1)(E_n+E_{n'}) \langle n|x^{k-2}|n'\rangle + k(k-1)(k-2)(k-3) \langle n|x^{k-4}|n'\rangle . \qquad (5.6)$$

Thus all higher moments for any particular transition of the quartic anharmonic or the pure quartic oscillator may be obtained in terms of the lowest non-zero moment of that transition. The initial requirements in these cases is effectively reduced to one moment because of the even

symmetry of the Hamiltonian, the other moment being zero. In Table (V.1) the ratio of the 01 element for the matrices x, x^5, ... x^{25} for the quartic anharmonic and the pure quartic oscillators are tabulated. For large k the recursions (5.5) and (5.6) yield

$$\lambda \langle n|x^k|n'\rangle / \langle n|x^{k-4}|n'\rangle \sim k^2, \quad k \to \infty \quad , \tag{5.7}$$

which describes the asymptotic behaviour of the moments in these cases.

V.2 Computation of the Transition Moments

The lower moments between various pairs of the anharmonic oscillator eigenstates may now be computed in the following manner. The expansion coefficients $\{a_m(E)\}$ for the required eigenfunctions are evaluated by substituting the corresponding computed eigenvalues in the recursion for $\{a_m(E)\}$. We include as many number of coefficients $\{a_m\}$ in the expansion of an eigenfunction as were required for obtaining the eigenvalue stable to 16 significant figures. The range of integration for the evaluation of the transition moments is truncated at $x = x_A$, the point in the non-classical region at which the computed eigenfunction just begins to increase in magnitude. Since the eigenvalues used are accurate to 15 significant figures, the computed

eigenfunctions reach extremely small values in the non-classical region before they finally start increasing in magnitude for large $|x|$ (see section II.5). The contribution to the transition moments from the rest of the configuration space is estimated to be $<O(10^{-14})$. Thus,

$$\langle n|x^k|n'\rangle = \sum_j \sum_{j'} a_j^{(n)} a_{j'}^{(n')} \int_{-x_A}^{+x_A} x^{k+j+j'} e^{-\{\alpha(n)+\alpha(n')\}x^2} dx \tag{5.8}$$

where $|n\rangle = \frac{1}{\sqrt{N}} \sum_j a_j^{(n)} e^{-\alpha(n)x^2}$, $|n'\rangle = \frac{1}{\sqrt{N'}} \sum_{j'} a_{j'}^{(n')} e^{-\alpha(n')x^2}$

N and N' are the normalization constants for the respective state. The integrals involved in (5.8) may be expressed in terms of the integrals $I_{2s}(\beta) = \int_0^1 x^{2s} e^{-\beta x^2} dx$, ($s$ = integer), which satisfy the recurrence relation (see Appendix B),

$$(2s-1)\, I_{2s-2}(\beta) - (2s+1+2\beta)\, I_{2s}(\beta) + 2\beta\, I_{2s+2}(\beta) = 0\ . \tag{5.9}$$

The actual procedure for the evaluation of $I_{2s}(\beta)$ is described in Appendix B. The computation of moments therefore requires no integration.

The non-zero matrix elements of x and x^2 in the lowest ten eigenstates of the quartic anharmonic and the pure quartic oscillators for $\lambda = 1$ were thus computed and are presented in Tables (V.2) and (V.3). Each moment given in the Tables

(V.2) and (V.3) has been checked by varying α in the appropriate range and is claimed to be accurate to all 12 figures given in tables. The transition moments for the quartic anharmonic oscillator are reported for the first time in this work. Among the earlier literature only a few non-zero moments for the pure quartic oscillator were evaluated to some accuracy (Chan and Stelman 1963, Reid 1970). The corresponding present values for the pure quartic oscillator moments are at least 5-6 figures more accurate. Further, the recursions (5.5) and (5.6) give all the higher moments to the same accuracy as of the lowest non-zero moment for that transition, without integration.

* * * * *

The work presented in this thesis forms a part of a paper entitled 'The Anharmonic Oscillator' accepted for publication in the Proceedings of the Royal Society.

TABLE (V.1) : The ratio $[\langle 1|x^k|0\rangle/\langle 1|x|0\rangle]$ for the Quartic Anharmonic and the Pure Quartic Oscillators from recursions (5.5) and (5.6).

k	$[\langle 1\|x^k\|0\rangle/\langle 1\|x\|0\rangle]$ The Pure Quartic Oscillator ($\lambda = 1$)	$[\langle 1\|x^k\|0\rangle/\langle 1\|x\|0\rangle]$ The Quartic Anharmonic Oscillator ($\lambda = 1$)
1	1.0	1.0
3	0.937 978 052 782 871	0.825 567 331 595 326
5	1.361 642 584 655 12	1.073 506 435 204 95
7	2.604 081 483 536 68	1.862 740 950 928 00
9	6.086 284 029 521 49	3.986 125 267 322 92
11	16.628 197 346 910 1	10.048 610 500 904 6
13	51.631 352 902 977 5	28.965 590 251 421 1
15	178.629 006 811 098	93.500 722 956 452 3
17	678.615 442 628 609	332.840 550 182 697
19	2 799.464 881 619 44	1 291.298 361 789 83
21	12 430.058 107 522 6	5 409.354 773 052 46
23	58 981.717 084 750 6	24 284.238 551 754 3
25	297 337.097 041 684	116 109.487 781 311

TABLE (V.2) : The Nonzero Matrix Elements $\langle n|x|n'\rangle$ and $\langle n|x^2|n'\rangle$ between the Lowest Ten Eigenstates of the Pure Quartic Oscillator ($H=p^2+\lambda x^4$, $\lambda=1$).

$\langle n|x|n'\rangle$

n \ n'	0	2	4	6	8
1	0.600 804 942 334	-0.734 340 765 283	0.037 148 575 006	-0.001 717 059 807	0.000 077 835 558
3	-0.052 461 289 392	0.838 905 284 915	-0.922 557 714 360	0.044 496 328 098	-0.002 017 187 983
5	0.001 526 391 867	-0.041 176 357 805	0.993 412 452 308	-1.055 437 316 854	0.049 916 105 158
7	-0.000 069 750 597	0.001 881 766 737	-0.047 366 390 038	1.110 946 312 523	-1.161 417 539 380
9	0.000 003 142 839	-0.000 084 789 094	0.002 134 420 225	-0.052 225 616 778	1.207 855 178 442

TABLE (V.2)(...Contd.)

$\langle n | x^2 | n' \rangle$

n \ n'	0	2	4	6	8
0	0.562 022 648 789				
2	-0.468 490 426 792	1.244 714 121 511			
4	0.053 785 987 462	-0.842 210 662 995	1.841 609 138 522		
6	-0.004 164 678 784	0.084 143 051 237	-1.142 351 998 243	2.352 866 384 212	
8	0.000 275 248 428	-0.006 092 887 947	0.109 046 749 878	-1.406 256 536 322	2.813 476 631 178

$\langle n | x^2 | n' \rangle$

n \ n'	1	3	5	7	9
1	0.901 605 895 819				
3	-0.669 891 863 409	1.557 909 193 537			
5	0.069 874 305 670	-0.998 136 794 911	2.105 010 651 065		
7	-0.005 181 476 175	0.097 059 890 197	-1.277 762 011 524	2.588 299 562 716	
9	0.000 351 500 121	-0.006 913 995 758	0.120 540 585 778	-1.529 062 457 270	3.029 980 037 256

TABLE (V.3) : The Nonzero Matrix Elements $\langle n|x|n'\rangle$ and $\langle n|x^2|n'\rangle$ between the Lowest Ten Eigenstates of the Quartic Anharmonic Oscillator ($H = p^2+x^2+\lambda x^4$, $\lambda = 1$).

n \ n'	0	2	4	6	8
1	0.552 565 959 314	-0.703 650 332 276	0.028 221 033 399	-0.001 112 357 680	0.000 044 353 181
3	-0.021 994 760 550	0.811 932 201 538	-0.898 030 313 847	0.033 573 628 574	-0.001 462 368 026
5	0.000 860 619 507	-0.032 880 475 307	0.970 612 527 510	-1.033 955 799 881	0.042 774 294 006
7	-0.000 034 133 433	0.001 304 148 899	-0.039 917 301 180	1.090 520 076 925	-1.141 862 823 393
9	0.000 001 367 233	-0.000 052 238 432	0.001 598 994 768	-0.045 341 606 849	1.189 039 213 297

TABLE (V.3)(...Contd.)

$\langle n | x^2 | n' \rangle$

n \ n'	0	2	4	6	8
0	0.305 813 650 718				
2	-0.406 699 817 397	1.155 440 519 200			
4	0.036 182 636 992	-0.780 963 812 311	1.750 939 501 751		
6	-0.002 348 407 804	0.065 980 790 644	-1.080 139 164 213	2.261 705 958 855	
8	0.000 134 089 031	-0.004 176 369 865	0.090 316 339 087	-1.343 508 993 975	2.721 984 850 987

$\langle n | x^2 | n' \rangle$

n \ n'	1	3	5	7	9
1	0.801 250 595 541				
3	-0.608 854 122 066	1.467 523 215 391			
5	0.052 155 623 899	-0.936 356 744 621	2.014 067 745 278		
7	-0.003 326 812 043	0.078 572 602 359	-1.215 261 195 461	2.496 957 081 437	
9	0.000 188 014 732	-0.004 952 669 142	0.101 419 574 690	-1.466 112 455 735	2.938 362 108 797

APPENDIX A

We describe here the procedure adopted for obtaining initial estimates of the eigenvalues in the 'boundary layer' when n is large. Let us suppose that the desired eigenvalue is E_n $(\lambda = \lambda_b)$, where (n, λ_b) **lies** in the 'boundary layer'. An initial estimate for it is obtained as follows:

(i) We first obtain accurate eigenvalue E_n $(\lambda = \lambda_0)$, where (n, λ_0) lies in the pure anharmonic region and the initial estimate for it is obtainable from the WKB formula.

(ii) The desired value $\lambda = \lambda_b$ is reached through a sequence of intermediate values $\{\lambda_i\}$, i = 0, 1, 2, ... The initial estimate for E_n $(\lambda = \lambda_{i+1})$ is obtained using accurate values of E_n $(\lambda = \lambda_i)$ and the Taylor series expansion. It gives

$$E_n^{\text{initial}}(\lambda_{i+1}) = E_n(\lambda_i) + (\lambda_{i+1} - \lambda_i)\left.\frac{\partial E_n}{\partial \lambda}\right|_{\lambda = \lambda_i}, \quad i=1,2,\ldots$$

where

$$\left.\frac{\partial E_n}{\partial \lambda}\right|_{\lambda = \lambda_i} \approx \frac{E_n(\lambda_i) - E_n(\lambda_{i-1})}{\lambda_i - \lambda_{i-1}}$$

The values $\{\lambda_i\}$ are chosen sufficiently close to each other so that $E_n(\lambda_{i+1})$ may be computed avoiding jumps to $E_{n\pm 1}(\lambda_{i+1})$.

(iii) $E_n^{\text{initial}}(\lambda_{i+1})$ is refined to 15-figure accurate eigenvalue $E_n(\lambda_{i+1})$ by the method used in this thesis (Section II.2).

(iv) Steps (ii) and (iii) are continued till the value $\lambda = \lambda_b$ is reached.

APPENDIX B

The recursive evaluation of the integrals defined by

$$I_{2s}(\beta) = \int_0^1 x^{2s} e^{-\beta x^2} dx \qquad (B.1)$$

is considered in this Appendix. On integrating (B.1) by parts, we obtain a following inhomogeneous recurrence relation

$$2\beta I_{2s+2}(\beta) - (2s+1) I_{2s}(\beta) + e^{-\beta} = 0. \qquad (B.2)$$

Rewriting (B.2) on replacing the index 's' by 's-2'

$$2\beta I_{2s}(\beta) - (2s-1) I_{2s-2}(\beta) + e^{-\beta} = 0 \qquad (B.3)$$

and eliminating the inhomogeneous part from (B.2) and (B.3), one obtains a 3-term homogeneous recurrence relation for $I_{2s}(\beta)$:

$$2\beta I_{2s+2}(\beta) - (2s+1+2\beta) I_{2s}(\beta) + (2s-1) I_{2s-2}(\beta) = 0. \qquad (B.4)$$

The integrals $I_{2s}(\beta)$ may therefore be computed for any value of s by successive application of the relation (B.4). However, since the computations are carried out perforce with rounded values, the relative errors grow and overtake the wanted function when a straightforward use of the above recursion

is made in forward direction (increasing s). This occurs when a recurrence relation has two independent solutions and the solution desired is diminishing as the index 's' increases, while the companion solution is increasing. On reversing the direction the roles of the two solutions are interchanged and the contribution of desired solution now increases while the unwanted solution diminishes (Abramowitz and Stegun 1965). Computation of the integrals $I_{2s}(\beta)$ is therefore done by applying the recursion (1.4) in backward direction (decreasing s). The recursion is started from a sufficiently higher index 's' using arbitrary starting values (Miller 1952). The values obtained in this manner differ from the desired solution by a constant multiplier which is calculated from the values of $I_o(\beta)$ obtained from the tables for the error functions.

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